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In-situ systems to accelerate the stabilization of waste deposits involve three essential elements: selection of a chemical or biological agent (reactant) which can react with and stabilize the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste.

Four reactant categories have been examined: biodegradation, surfactant-assistant flushing, hydrolysis, and oxidation. Of these, biodegradation and surfactant-assisted flushing appear most promising as in-situ treatment techniques. For any treatment technique, the potential toxicity of the applied reactant and any intermediate compounds or by-products must be carefully evaluated.

Methods of delivery of reactants based upon gravity include surface flooding, ponding, surface spraying, ditching, and subsurface infiltration beds and galleries. Forced injection (pumping) may also be used. Permeability is an important consideration in selecting the delivery system. Recovery systems using gravity include open ditching and buried drains, and pumped methods include wellpoint and deep well systems. Basically, the same limitations that apply to delivery systems are also true for recovery systems.

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SYSTEMS TO ACCELERATE IN SITU STABILIZATION OF WASTE DEPOSITS

by

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This report is intended to present information on the potential application of a number of in situ treatment technologies for the stabilization of deposits containing various organic waste compounds. It is not intended to address every conceivable waste type or all possible applications of the technologies described. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environment and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the important elements of technology which need to be understood and applied in order to accomplish an effective in-situ stabilization of hazadous wastes on an uncontrolled waste site. This will be useful to remedial action plan designers and plan approval staffs in clarifying the advantages and disadvantages of various in-situ stabilization technologies with respect to pollutant, site, and technology interreactions. For further information the reader should contact the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Research Laboratory

PREFACE

This report covers a broad area of potential in situ surface and subsurface remediation activities at uncontrolled waste sites. Conventionally, remediation has been conceived of as containment and isolation, or as excavation followed by secured landfill deposition or incineration. These two "conventional" methods may not always be practicable or economically achievable, especially where contamination of a large area has occurred. Furthermore, the waste material is not necessarily destroyed; thus objections to these methods have arisen based upon the long lifetimes of many hazardous wastes in the environment and the undemonstrated longterm reliability of engineered safety measures.

The application of in situ systems to accelerate the stabilization of waste deposits offers a potential solution to the concerns raised with respect to conventional approaches. The fundamental concept for in situ stabilization is chemical treatment of the waste within the soil medium. This requires the use of a treatment agent (reactant), a means for delivering the reactant to the waste and usually a means for recovering the products of the reaction. This three part concept -- delivery, recovery and treatment selection -- is discussed in this report. In situ treatment may be used in concert with other remedial actions. For example, excavation and treatment on the surface (incineration, soil washing) may be used for the most highly concentrated source materials, followed by in situ treatment of the plume or other remaining, less-contaminated areas.

It is important to note that while each individual step of the basic in situ treatment process is part of a broad body of technical experience, the combination of injection, reaction and recovery as a system for in situ remediation has scarcely been practiced and is in its infancy as an integrated technology. This finding frustrates efforts to systematize selection of reactant, delivery and recovery systems because of the near absence of proven field experience. One danger of which the reader must be clearly forewarned is that a report such as this, which attempts to systematize the process of selecting an in situ treatment system, may appear to promise too much in terms of specificity and definition and may appear to suggest that firm solutions exist. To underscore this, the authors note that, at best, application of systems to accelerate the in situ stabilization of waste deposits is in its early stage of development. Further, the application of these systems to uncontrolled waste sites will require a site-by-site, customized approach since the subsurface geohydrology, waste inventory and site history will be unique for each site, a situation defying systematization. There is also extensive need for laboratory simulations and testing prior to implementation of in situ systems. Data are too scarce to predict, with confidence, the efficiency and practicality of the methods. However, the data at this stage in the evolution of these technologies can justify the development of general guidelines. This report provides the general guidelines and the basis for them. It also serves as a starting point for developing the site specific requirements for implementation of in situ systems to accelerate the stabilization of waste deposits, and for identifying future research and investigation needs in this area.

ABSTRACT

In situ systems to accelerate the stabilization of waste deposits have been presented as alternatives to containment, isolation or excavation as methods for remediation of uncontrolled waste sites. In situ applications involve three essential elements: selection of a chemical or biological agent (reactant) which can react with and stabilize the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste. The most promising applications for in situ treatment methods are for spill or plume types of contamination, where the contaminants are relatively evenly distributed and preferably in liquid form. Delivery of reactants to solid, heterogeneous, low permeability deposits will be more difficult. In situ methods may find particular application when used in combination with other remedial measures, for example, removal of the source material and in situ treatment of the plume.

Four reactant categories have been examined: biodegradation, surfactant-assistant flushing, hydrolysis, and oxidation. Of these, biodegradation and surfactant-assisted flushing appear most promising as in situ treatment techniques. For any treatment technique, the potential toxicity of the applied reactant and any intermediate compounds or by-products must be carefully evaluated. Furthermore, the potential for undesirable reactions with other contaminants present must be studied (e.g., oxidation of phenol with hydrogen peroxide may also oxidize chromium (III) to the more toxic hexavalent chromium).

Methods of delivery of reactants based upon gravity include surface flooding, ponding, surface spraying, ditching, and subsurface infiltration beds and galleries. Forced injection (pumping) may also be used. Permeability is an important consideration in selecting the delivery system. Gravity delivery methods require a permeability of the soil/waste medium in the range 10^{-1} cm/sec to 10^{-3} cm/sec (280 to 2.8 ft/day). Forced injection is most effective at a permeability in the range of 10^{-1} cm/sec to 10^{-4} cm/sec

(280 to 0.28 ft/day); below this permeability limit a potential application offorced injection for reagent delivery coupled with electro-osmosis for recovery may exist. Additionally, gravity systems should be considered only when the waste deposit lies in the unsaturated zone and when the depth to the bottom of the deposit is less than 5 meters (16 feet). Otherwise, forced injection should be considered.

Recovery systems using gravity include open ditching and buried drains, and pumped methods include wellpoint and deep well systems. Basically, the same limitations that apply to delivery systems are also true for recovery systems. Gravity-induced recovery works best when the water table is within 5 meters (16 ft) of the surface. For depths in the range of 0-8 meters (0-26 ft), well points can also be considered. Depths greater than the suction limit (about 8 meters or 26 ft in practice) will require the use of down-hole pumps for recovery.

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SECTION 1

DELIVERY AND RECOVERY SYSTEMS FOR WASTE DEPOSIT STABILIZATION

In order to remediate waste deposits in situ, reactants (chemical, biological or both) must be delivered to the waste deposit and surrounding soil containing the contaminants. During or following treatment, spent reactants or stabilization by-products may require removal from the waste deposit and the surrounding soil. This section provides information currently available concerning the various aspects of delivery and recovery systems usable for in situ stabilization. Sections 2-5 provide information currently available on the biological and chemical processes and reagents that may be applicable to waste deposit stabilization. Section 6 integrates all of the foregoing, to establish guidance concerning the use of stabilization technologies at specific sites.

The specific objectives of Section 1 are to:

1. Identify and review the various soils engineering parameters affecting the selection and application of delivery and recovery systems (Section 1.1)

2. Review the types and features of various gravity and forced delivery systems (Section 1.2)

3. Review the types and features of various gravity and forced recovery systems (Section 1.3)

4. Review delivery and recovery enhancement technology available through electro-osmosis (Section 1.4)

5. Present a comparative analysis of alternative delivery and recovery systems (Section 1.5).

1.1 Engineering Features and Geohydrologic Parameters

1.1.1 Introduction

An evaluation of potential delivery and recovery methods which could be employed for in situ treatment of waste deposits must consider the physical setting of the waste deposit in terms of its relationship with the subsurface soil and groundwater, and the geohydrologic parameters of the waste deposit and surrounding soil media. In theory, there are numerous possible combinations of settings and geohydrology which could arise. The following assumptions were made in order to confine the discussion to the most common situations likely to be encountered:

- Waste deposits are in a solid state and no immiscible flow is expected.

- Waste deposits are located within the upper unconsolidated formation (above or below the groundwater table) and are not present in a confined aquifer or bedrock.

- Recovery of the reaction products and spent reactant will be exclusively from a water table aquifer.

- Solutions applied will have physical characteristics similar to water and precipitates which may form will not significantly affect deposit porosity and hydraulic conductivity.

Based on an understanding of the geohydrology of the site it may be determined that it is necessary to completely contain the waste deposit and any leachate generated, or place a hydrologic barrier downgradient of the deposit to assist the recovery system. Grout curtains, slurry walls, and sheet pilings have been used for this purpose. A description of these methods is beyond the scope of this work, but is contained in companion documents to this report, including A W Martin Associates (1978), A D Little (1983), USEPA (1984a), Spooner et al. (1984), and Repa and Kufs (1985).

1.1.2 Waste Deposit Settings and Methods of Delivery and Recovery

Given the above assumptions, four basic methods (and combinations thereof) have been investigated and conceptually applied as possible delivery and recovery systems. These are:

- Gravity delivery by surface or subsurface means
- Forced delivery
- Gravity recovery
- Forced recovery.

These four methods are briefly discussed in the following paragraphs.

1.1.2.1 Gravity Delivery

Gravity delivery can be applied in cases where the waste deposit is present either partially above or below the natural ground level, or completely below the natural ground level and overlain by a permeable material. The qualitative factors that would give preference to the use of gravity delivery systems include:

- Shallow depth to waste deposit from the surface (less than 5 meters or 16 feet)

- Highly permeable cover material between land surface and the waste deposit (greater than 10^{-3} cm/sec or 2.8 ft/day)

- Highly permeable waste deposit and surrounding soil media (greater than 10^{-3} cm/sec or 2.8 ft/day)

- Waste deposit located above the groundwater table

- High surface soil infiltration rate (greater than 10 cm or 4 inches per day)

- Availability of a relatively long treatment time (i.e., months to years).

Gravity delivery can also be applied, however, in cases where the subsurface deposit is overlain by an impermeable cover if the impermeable layer can be cost-effectively removed, or subsurface methods of gravity delivery (e.g., infiltration galleries) are employed, thus eliminating the need for extensive excavation of the impermeable cover.

1.1.2.2 Forced Delivery

Forced delivery methods can be used in all the conditions noted above, but may not be suitable in some cases of surficial or very shallow waste deposits (forced injection of a fluid into a very shallow deposit could lead to soil cracking caused by excessive uplift pressures, leakage to the surface, etc). However, shallow injection well points can be used for some shallow waste deposits.

1.1.2.3 Gravity and Forced Recovery

Recovery system feasibility is significantly affected by depth to the waste deposit and by the geohydrologic properties of the waste deposit and surrounding soil media. Gravity recovery is most suited to shallow waste deposits (less than 10 meters or 33 feet deep, and less than 5 meters or 16 feet below the water table) with hydraulic conductivities of 10^{-3} cm/sec (2.8 ft/day) or greater. Forced recovery is generally required for deeper deposits or less permeable conditions.

1.1.3 Geohydrologic Parameters

The geohydrologic parameters of the waste deposit and surrounding soil media which can have an effect on the selection of delivery and recovery systems are:

- Surface soil infiltration rate

- Hydraulic conductivity of the waste deposit, cover material and surrounding soil media
- Interrelated parameters of porosity, specific yield, specific retention and grain size distribution of the host soils and waste deposit.

Detailed descriptions of the methods for measuring and evaluating these parameters during site investigations, and their use in evaluating site geohydrology, are contained in Freeze and Cherry (1979), USEPA (1980a), USEPA (1980b), and Repa and Kufs (1985). The following brief discussion of these parameters, however, is provided.

1.1.3.1 Infiltration Rate

The infiltrative capacity of the surface soil above a waste deposit can be a limiting parameter to the rate at which reactants can be applied by surface gravity delivery methods. The infiltration rate of the soil is defined as the rate (cm/min) at which water (or other fluid) enters the soil through its surface. The infiltration rate is a function of both texture and structure of the soil as well as moisture content. For example, the drier the soil profile, the higher the infiltration rate. Conversely as the soil pores fill with fluid, the infiltration rate will decrease until an approximate steady-state condition is approached. Usually the steady-state infiltration rate is used as the design criterion for the hydraulic loading rate of surface delivery methods. Thus, it is necessary to know the cumulative water intake of a soil column as a function of time to be able to calculate the fluid application rate required for treatment of the waste deposit. If the natural infiltration rate is too low, it can be increased by tilling the surface (USEPA, 1984b).

The equation for expressing the short-term change in infiltration rate is approximated by:

$$I_o = A_I t^n \qquad (1\text{-}1)$$

where: I_t = infiltration rate at time, t (length/time)

A_I = a constant representing the instantaneous intake rate at time equal 1 minute

n = an exponent which, for most soils, is negative with values between 0 and -1

t = time

The equation for expressing the cumulative intake of fluid at time, t, is:

$$Y = A_I t^{(n+1)}/(n+1) \tag{1-2}$$

where: Y = cumulative intake (length) and other parameters are as defined above

The coefficients needed for computation in the above equations can be secured from data obtained in field infiltrometer studies. The field determined values for (Y) and (t) can be plotted on log-log paper with the slope of the line of best fit equal to n+1. The coefficient A may be calculated from equation 1-2 using any point (t,Y) on the line.

Methods and tools which can be used to determine infiltration rates in the field are basin flooding, sprinkler infiltrometers, cylinder infiltrometers, and lysimeters (Bouwer, 1964; Bouwer, 1966; Bouwer and Rice, 1967). Basin flooding involves using an area ranging from 1 m^2 (10 ft^2) to 0.1 hectare (0.25 acre), flooding it with water, and measuring the infiltration rate (USEPA, 1977). Sprinkler infiltrometers are used primarily to determine the limiting application rate for systems using sprinklers. Cylindrical infiltrometers and lysimeters are most commonly used. The cylinder infiltrometer technique involves driving a metal cylinder into the soil to a depth of about 15 cm (6 inches). The cylinder is usually 15-35 cm (6 to 14 inches) in diameter and 25 cm (10 inches) long. A buffer zone around the cylinder is formed either by diking or placing another cylinder around the first one. The buffer zone serves to prevent lateral flow of water from the inner cylinder. Water is then introduced into the inner cylinder until a steady-state condition is reached, while the water level in the buffer zone is kept at the same level. A lysimeter test involves the recovery of an undisturbed soil core sample whose infiltration rate is measured in the laboratory. The field implementation, methods of calculation, theoretical background, limits of applicability and potential problems associated with these methods are discussed in greater detail in Meinzer (1923), USEPA (1977), USEPA (1980a), and Freeze and Cherry (1979).

In all cases the infiltration tests should be performed with the solution which will actually be used during the in situ treatment process. This is preferable because the physical and chemical properties of the solution (density, viscosity, ionic strength, adsorption properties) may alter the value of the infiltration rate compared to that determined using water alone.

1.1.3.2 Hydraulic Conductivity

Hydraulic conductivity (K) is defined by Darcy's law in the equation:

$$Q = KIA, \text{ or} \tag{1-3}$$

$$v = KI = Q/A, \tag{1-4}$$

where: Q = flow rate (length^3/time)
K = hydraulic conductivity (length/time)
I = hydraulic gradient (dimensionless)
A = cross-sectional area (length^2)
v = specific discharge ("Darcy velocity") (length/time)

The actual flow velocity of groundwater or a conservative (i.e., not attenuated) contaminant is given by:

$$V = KI/n_{eff} = v/n_{eff} \tag{1-5}$$

where n_{eff} = the effective porosity for flow of the medium (i.e, excluding "dead end" pores through which the fluid will not flow).

In coarse-grained materials, n_{eff} is close to the specific yield (see below). However, n_{eff} in fine materials may be much lower than the specific yield. If either the total porosity or specific yield is used to calculate V, erroneously low estimates of velocity may result (Bear, 1979; Gibb et al., 1985).

Values of hydraulic conductivity (K) depend on properties of the fluid (such as viscosity) as well as that of the porous medium. In general, the hydraulic conductivity is anisotropic, i.e., the K for horizontal flow (K_h) is not equal to the K for vertical flow (K_v). The hydraulic conductivity K can also be expressed by (Luthin, 1957):

$$K = C(d_{50})^2 pg/u \tag{1-6}$$

where:

C = proportionality constant for the medium, based on geometric characteristics (dimensionless)
d_{50} = mean grain diameter of the medium (length)
p = density of the fluid (mass/length^3)
u = kinetic viscosity of the fluid (mass/length x time)
g = acceleration of gravity (length/time^2)

In this equation $Cd_{50}{}^2$ (also defined as k, the specific or intrinsic permeability) is a function of the medium alone, while pg/u is a function of the fluid alone. The hydraulic conductivities for fluids other than water can be estimated using these relationships and the other fluids' viscosities and densities.

Hydraulic conductivity does not remain constant but may vary over time, for example, from increased swelling of soil clay particles, change in pore size distribution or change in the chemical nature of the soil-water interactions.

In particular, the addition of chemical reagents during in situ treatment may significantly alter this value. It is therefore important to evaluate the hydraulic conductivity under conditions of reactant saturation.

Obtaining a representative value of the hydraulic conductivity at a particular site is essential to establish the rate at which a treatment solution can move through the waste deposit and surrounding soil media. Not only is it important to obtain hydraulic conductivity of the medium but the hydraulic conductivity of the waste deposit must also be determined. The relationship between the K values of the host material and the waste material will dictate which delivery or recovery methods may be applicable and effective. For example, attempting to deliver a fluid by gravity into a waste and host material both with hydraulic conductivities of 1×10^{-3} cm/sec (2.8 ft/day) would normally be feasible; however, if the waste material is surrounded by a host material with a hydraulic conductivity of 1×10^{-2} cm/sec (28 ft/day), the fluid will try to follow the path of highest hydraulic conductivity (path of least resistance) and travel within the host material, not effectively entering and permeating the waste deposit.

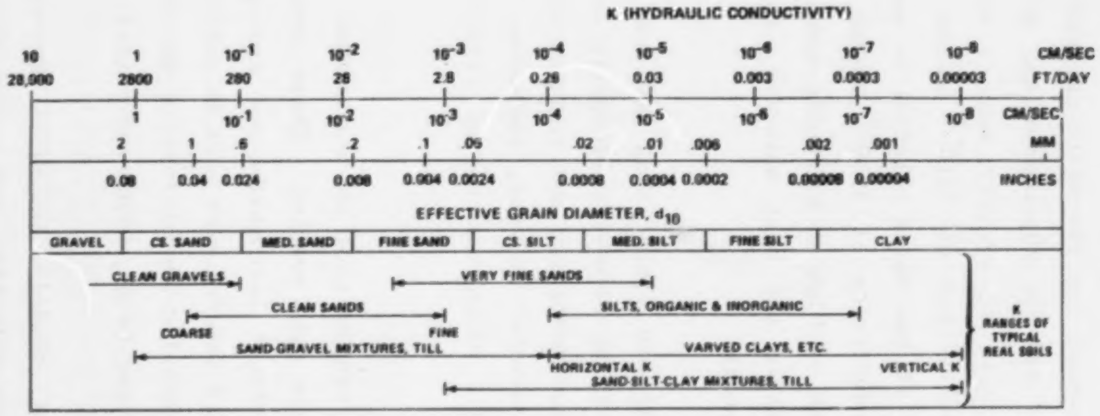
Several methods, including laboratory and field (slug and pump) tests, that can be employed to obtain a value for the saturated hydraulic conductivity of a particular medium. The theory, implementation and interpretation of these methods are described in detail in several sources, including USEPA (1977); USEPA (1980a), Repa and Kufs (1985), Olson and Daniel (1981), Freeze and Cherry (1979) and Luthin (1957).

Laboratory tests using permeameters can be made on undisturbed core samples taken in the field with an appropriate core sampler. These methods give the vertical hydraulic conductivity. Although inexpensive and conceptually easy, laboratory hydraulic conductivity tests require much care to achieve accuracy. Furthermore, laboratory determined hydraulic conductivities may not agree with field measurements from the same location (e.g., Olson and Daniel, 1981).

Hydraulic conductivity can also be crudely estimated according to the effective grain size of a soil. The effective grain diameter (d_{10}) means that 10 percent (by weight) of the soil particles are finer than the specified diameter. Table 1-1 shows that, for example, media with effective grain size (d_{10}) between 0.6 to 0.1 mm (0.02 to 0.004 inches) will have a hydraulic conductivity between approximately 1×10^{-1} and 1×10^{-3} cm/sec (280 and 2.8

TABLE 1-1

HYDRAULIC CONDUCTIVITY, POROSITY AND DRAINAGE CHARACTERISTICS OF MATERIALS (USEPA, 1980b)


K (HYDRAULIC CONDUCTIVITY)
10
28,000
1
2800
10^{-1}
280
10^{-2}
28
10^{-3}
2.8
10^{-4}
0.28
10^{-5}
0.03
10^{-6}
0.003
10^{-7}
0.0003
10^{-8}
0.00003
CM/SEC
FT/DAY
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
CM/SEC
2
1
.6
.2
.1
.05
.02
.01
.006
.002
.001
MM
0.08
0.04
0.024
0.008
0.004
0.0024
0.0008
0.0004
0.0002
0.00008
0.00004
INCHES
EFFECTIVE GRAIN DIAMETER, d_{10}
GRAVEL
CS. SAND
MED. SAND
FINE SAND
CS. SILT
MED. SILT
FINE SILT
CLAY
CLEAN GRAVELS
VERY FINE SANDS
CLEAN SANDS
COARSE
FINE
SILTS, ORGANIC & INORGANIC
SAND-GRAVEL MIXTURES, TILL
VARVED CLAYS, ETC.
HORIZONTAL K
VERTICAL K
SAND-SILT-CLAY MIXTURES, TILL
K RANGES OF TYPICAL REAL SOILS

	AVERAGE K VALUES	
Type	cm/sec	ft/day
very fine sand	5×10^{-3}	14
fine sand	2×10^{-2}	57
concrete sand	2×10^{-2}	57
fine to medium sand	5×10^{-2}	140
medium sand	10^{-1}	280
medium to coarse sand	1.5×10^{-1}	425
clean gravel	10	2.8×10^{4}
concrete gravel	25	7.1×10^{4}

RANGE OF POROSITY VALUES FOR VARIOUS MATERIALS

Type	Porosity (%)
clay	45 - 55
sand	35 - 40
gravel	30 - 40
sand and gravel	20 - 35
municipal waste	30 - 40

ft/day). Media with d_{10} between 0.1 to 0.005 mm (0.004 to 0.0002 inches) will have a hydraulic conductivity between $1x10^{-3}$ and approximately $1x10^{-6}$ cm/sec (2.8 to 0.003 ft/day).

The field bore-hole method or single well pump test is a commonly used method for measuring the in situ hydraulic conductivity of saturated soils. It is considered to be the simplest and most reliable of the available methods. Studies conducted through the years demonstrate that this method primarily measures the horizontal component of the hydraulic conductivity. The hydraulic conductivity can also be determined in the field by pumped-well aquifer tests using a series of wells. This method involves discharging or recharging one well at a known rate and measuring the response of water levels in the observation wells. Water level responses are then mathematically related to the hydraulic conductivity (Lohman, 1979; Freeze and Cherry, 1979; Repa and Kufs, 1985). Typical hydraulic conductivities of various soil materials are listed in Table 1-1.

Methods are also available for measuring the vertical hydraulic conductivity in the unsaturated zone. These include the double-tube method, the gradient intake method, and the use of an air entry permeameter. Detailed discussions of principles and equipment involved in each of these methods can be found in Bouwer (1964, 1966), Bouwer and Rice (1967), and Black (1965).

1.1.3.3 Specific Yield, Specific Retention, Porosity and Grain Size Distribution

Porosity is important in determining the quantity of fluid which can be physically accommodated by the media during delivery, and the velocity of groundwater (or reactant) flow through the media. Specific yield and specific retention values are important properties for modeling groundwater flow. In addition, these parameters indicate how much of the delivered reactant will remain within the soil or waste deposit, and how much will be released. An important consideration is that these parameters should be determined for the waste deposit in addition to the surrounding soil, since the waste deposit may control the maximum application rate and flow rate.

The specific yield of soil (with respect to water) is defined as the volume of water which will drain by gravity from a saturated soil sample, divided by the total volume of the soil sample. For relatively coarse-grained materials (sands and gravels), the specific yield is approximately equal to the effective porosity for flow (see Equation 1-5). The specific yield is expressed as a percentage (Johnson, 1967):

$$S_y = 100\ (V_w/V_s) \tag{1-7}$$

where: S_y = specific yield (dimensionless)
V_w = volume of liquid removed by gravity (length^3)
V_s = volume of soil (length^3)

The specific retention of soil with respect to water is defined as the volume of water which will be retained in an initially saturated soil sample against the pull of gravity, divided by the total volume of the sample. It is expressed as a percentage (Johnson, 1967):

$$R = 100(V_r/V_s) \tag{1-8}$$

where: R = specific retention (dimensionless)
V_r = volume of water retained by the soil against the pull of gravity (length^3)
V_s = volume of soil (length^3)

Porosity (n) can be defined as the ratio of the aggregate volume of the interstices (pores) of the rock or soil sample to its total volume. It can be expressed as a percentage by the following equation (Johnson, 1967):

$$n = 100\ (V_w/V_s) = 100\ (V_s - V)/V_s \tag{1-9}$$

where: n = total porosity (dimensionless)
V_s = total volume of soil or rock (length^3)
V_w = volume of water required to saturate the sample (length^3)
V = aggregate volume of the solid particles that make up the sample (length^3)

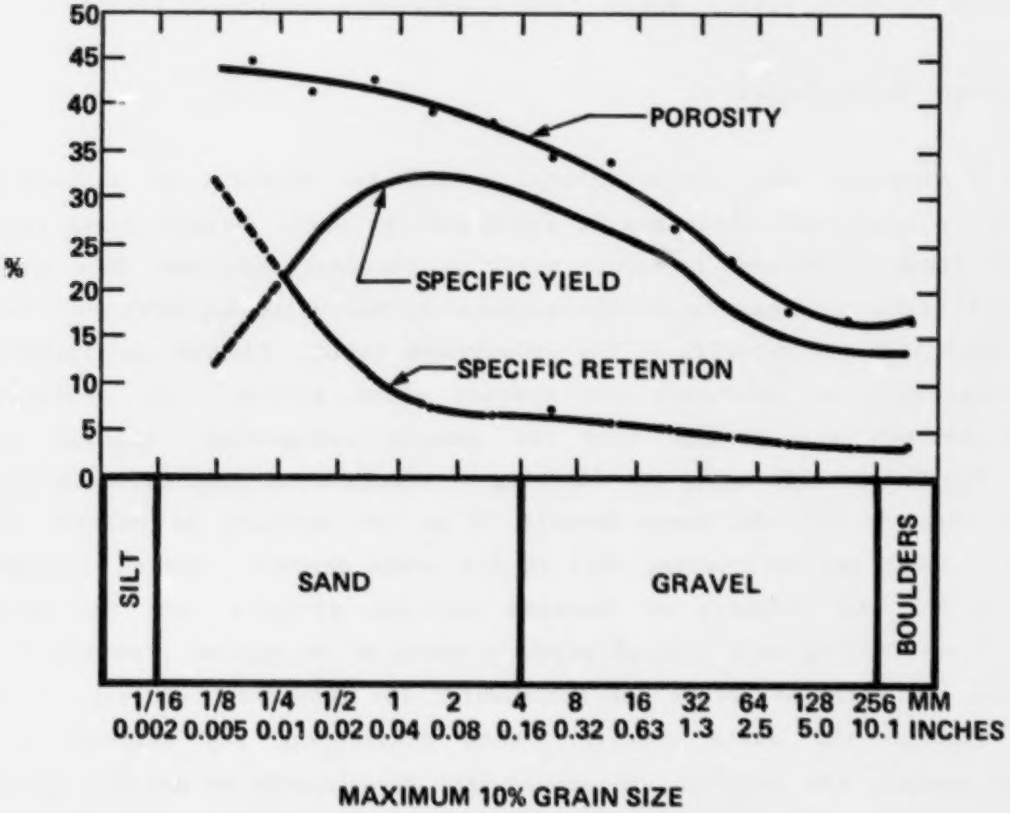
The porosity of a sample is best measured in the laboratory. Gibb et al. (1985) describe experiments to measure the effective porosity (n_{eff}) in geologic materials. It can also be estimated using a grain-size distribution curve (e.g., USEPA, 1977). Typical porosities of various soil materials are listed in Table 1-1. An example of the relationship between porosity, specific yield and specific retention according to grain size is shown in Figure 1-1.

Various laboratory and field test methods have been developed to determine porosity, specific yield and specific retention. These are reviewed in Johnson (1967), USEPA (1977), Bouwer (1978) and Freeze and Cherry (1979).

1.2 Delivery Technologies

Delivery techniques used for artificial groundwater recharge or wastewater treatment by land application may be applicable to waste deposit remediation efforts. These techniques introduce water or reactant solutions into waste deposits in order to react with contaminants in the waste deposits or flush contaminants from the deposits to the groundwater table. Flushed contaminants can subsequently be collected and treated above ground. The available delivery methods are grouped into two generic categories: gravity and forced. Gravity methods apply the flushing or reactant solution directly over the waste deposit (if the waste deposit is at the surface) or deliver the solution through the surrounding soil to the waste deposit. Forced delivery methods inject the flushing or reactant solution directly into the waste deposit or surrounding soil through pipes by means of an applied pressure. In both cases the solution enters the groundwater for subsequent recovery after passing through the waste deposit. When considering any delivery (or recovery) method, the reactant and groundwater flow should be modeled (using conventional flow net analysis or mathematical models) so that design parameters can be tested and proper delivery of reactant and recovery of spent solution can be assured. Groundwater flow analysis is described in most groundwater texts, including Freeze and Cherry (1979) and Cedergren (1977), and mathematical modeling is reviewed in Wang and Anderson (1982).

FIGURE 1-1
POROSITY, SPECIFIC RETENTION AND SPECIFIC YIELD VARIATIONS WITH GRAIN SIZE



NOTE: SOIL SAMPLE FROM SOUTHERN COASTAL BASIN, CA, CLASSIFICATION SHOWN IS THE LABORATORY CLASSIFICATION OF THE SAMPLE.

SOURCE: US EPA, 1977

The following sections present discussions of the design considerations of the following delivery technologies:

- Gravity
  - Flooding
  - Ponding
  - Spray Irrigation
  - Ditches
  - Subsurface Spreading (infiltration galleries and beds)
- Forced
  - Injection Wells

1.2.1 Gravity Delivery Methods

Gravity delivery methods are applicable at or near the ground surface and can be classified into two groups: surface and subsurface spreading. Surface spreading involves the application of the flushing or reactant solution over the waste deposit or overlying soils. Subsurface spreading requires the distribution of the flushing or reactant solution through the use of infiltration galleries or beds. The selection of a gravity delivery method depends on the following four factors:

Infiltration Rate and Soil Hydraulic Conductivity - The infiltration rate of the surface soil and hydraulic conductivity of the waste deposit and overlying soil affects the volume of solution that can be applied by gravity delivery methods. The infiltration rate can be increased by surface soil preparation (i.e., tilling), but increasing the hydraulic conductivity of subsurface materials is generally difficult or impossible.

Location of the Waste Deposit - Location of the waste deposit with respect to the ground surface and water table affects the selection of a gravity delivery method. If the waste deposit is exposed at the surface, then surface application methods such as flooding, spraying and ponding can be considered.

As the depth to the top of the waste deposit increases, the effectiveness of surface application is reduced because of lateral spreading or attenuation of the applied solution. If the waste deposit is located below the groundwater table, surface application will not be successful because the applied solution will be diluted, and not readily penetrate the water table to reach the waste deposit (although if its density is significantly greater than that of groundwater penetration may occur).

Topography -- The topography of the waste disposal site is a primary factor in the selection of a delivery method. Flooding or ponding should only be considered for terrain with slopes less than 3%. Trenching or ditching would be more effective for topography characterized by slopes greater than 3%.

Climate - The climatological influences at a site affect the selection of gravity delivery methods. Of particular importance are frost penetration depth and groundwater level variations (caused by seasonal changes or tidal effects).

1.2.1.1 Selection of Gravity Delivery Methods

In developing the selection methodology for gravity delivery methods, it is assumed that the deposit will be completely saturated with the applied solution, and the applied solution will be recovered by interception of the water table, i.e., gravity recovery (this assumption is necessary for calculation of required application rates).

Before selecting a gravity system, the following conditions must be known about the site:

- Surface topography and area of the site
- Sustained infiltration rate (I)
- Configuration of the waste deposit
  - areal dimensions (LxW)
  - thickness of deposit (d)
  - depth to deposit (d_o) from the surface

- Aquifer thickness (above impermeable layer) before solution application (H_d)
- Hydraulic conductivity (K) of the waste deposit and surrounding soil media (based on minimum value)
- Depth to water table (S_o) from the surface
- Porosity (n) based on maximum value.

Once these parameters are known the required application rate and the application rate attainable by gravity methods can be calculated to determine whether gravity delivery methods are viable.

1.2.1.2 Determination of the Required Application Rate

To satisfy the treatment objectives of complete saturation of the waste deposit and required detention time, a solution should be applied at a certain rate. For gravity recovery (using a drain or buried pipe placed perpendicular to groundwater flow) this rate can be determined by using the following equation (USEPA, 1977; Huisman and Olsthoorn, 1983) (see Figure 1-2):

$$q_1 = K (H_c^2 - H_d^2) / L (L + 2X) \tag{1-10}$$

where:

H_c = Total saturated thickness above aquiclude required to meet the assumption that the waste deposit is fully saturated (length)

H_d = Elevation of the recovery system above the impermeable layer (i.e., the original water table elevation before solution application) (length)

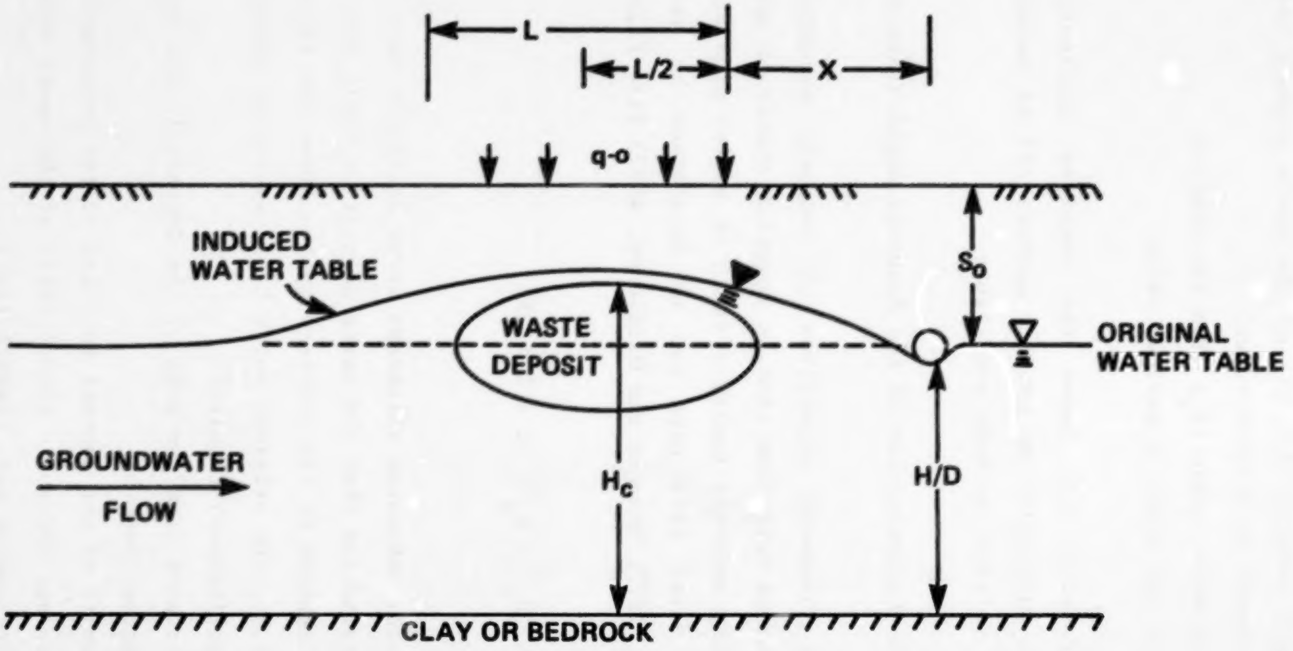
X = Distance from the edge of the deposit to the recovery system (length)

L = Length of the deposit parallel to the groundwater flow (length)

K = Average hydraulic conductivity of the waste deposit and surrounding soil (length/time)

q_1 = Required application rate per unit area of the deposit to satisfy the saturation criterion (length/time).

FIGURE 1-2
GENERAL LAYOUT OF A GRAVITY DELIVERY
AND RECOVERY SYSTEM


L
L/2
X
q-o
INDUCED
WATER TABLE
S_o
WASTE
DEPOSIT
ORIGINAL
WATER TABLE
GROUNDWATER
FLOW
H_c
H/D
CLAY OR BEDROCK

In this equation (USEPA, 1977) all values except q_1 and X are measured. The application rate, q_1, multiplied by the area of application (L x W) represents the total flow of solution through the saturated waste deposit and surrounding soil to the recovery system which is located at a distance, X, from the edge of the waste deposit. For continuous in situ treatment operation, the unit flow rate, q_1, is also the required recovery rate to maintain the treatment processes in a stable, steady state condition. Assuming a reasonable distance of X for the recovery system from the edge of the waste deposit, the application rate, q_1, can be estimated by solving equation (1-10).

Another equation expresses the relationship between the application rate (q_1), time (t) required for saturation of the waste deposit and surrounding soil media, and the location of the recovery system (X) as follows:

$$t = n\,(H_c + H_d)\,X/2q\,W \qquad (1\text{-}11)$$

where:

t = time required for saturation of waste deposit and surrounding soil media (time)
n = porosity (dimensionless)
w = width of deposit perpendicular to groundwater flow

and other parameters are as defined above.

1.2.1.3 Determination of the Maximum Application Rate by Gravity Methods

The amount of solution that can be introduced into a deposit by gravity delivery methods depends on the area of application (wetted area) and its sustained infiltration rate (assuming either that the deposit is at the surface, or the infiltration rate is less than the hydraulic conductivity of the subsurface soil so that the hydraulic conductivity is not a limiting factor). For spraying or surface flooding, the area of application is determined by the areal extent of the waste deposit. The total amount of solution (Q_o) that can infiltrate into the deposit would be:

$$Q_o = AI_s \tag{1-12}$$

where: Q_o = maximum application rate of the deposit ($\text{length}^3/\text{time}$)
A = area of application (length^2)
I_s = sustained infiltration rate (length/time)

The results of this equation should be compared to equation (1-10) to check that the hydraulic conductivity of any soil layers between the surface and the waste deposit is not rate-limiting.

For application using ditches Q_o will depend on the wetted area (sides and bottom) of the ditch and the sustained infiltration rate through the wetted area at a particular level of solution in the ditch. This can be calculated if the infiltration rates through the ditch sides and bottom are determined in field pilot studies (or assumed to be the same as the soil infiltration rate). For application using ponds, infiltration beds or galleries, the soil permeability will be the rate-limiting parameter. In this case, the equation for delivery rate of solution would be Darcy's law (Equation 1-3) where A = area of bottom of the pond, infiltration beds or galleries.

The parameter q_o (= Q_o/A, the application rate per unit area of the delivery system) represents the surface infiltration or subsurface delivery rate (using Equation 1-3) achievable by a gravity delivery method. If q_1 is set equal to q_o in Equation (1-10), solving for X will define the minimum distance at which to locate the recovery system for the shortest treatment pathway and the minimal treatment time.

To achieve saturation, which is a basic assumption for this methodology, q_o must be equal to or greater than q_1. If q_o is less than q_1, the next step would be to determine whether q_o can be increased. Such increase could be effected by increasing applied head of the solution, varying soil and waste properties by tilling (USEPA, 1977), or introducing forced delivery systems.

1.2.1.4 Surface Applications

Flooding -- In effecting solution application by flooding, the solution is spread over the land surface in a thin sheet. This technique is similar to the flooding that is practiced as an irrigation method for agricultural land. It is also used as a method of artificial recharge for aquifers located near the ground surface. The method is effective and of low cost in areas which are flat or gently sloped (generally less than 3 percent slope) and uniform (gullies or ridges are absent) (ASCE, 1972), the waste deposit is at or near the surface, and soil and waste deposit infiltration and hydraulic conductivity are high (greater than 10^{-3} cm/sec or 2.8 ft/day). Preferred soil and waste deposit conditions are those similar to sands (SW), loamy sands (SM-SW), and sandy loams (SM) (ASTM, 1969).

Design parameters utilized for infiltration-percolation systems for wastewaters can also be applied to surface flooding systems. As seen in Table 1-2, an application rate of 300 cm (120 inches) per week is possible when waste deposit and surrounding soil characteristics are similar to those of sandy soils. This would be the equivalent to approximately 5200 m^3/per hectare (560,000 gallons per acre) per day.

In flooding applications, ditches can be used to distribute the solution across the up-slope end of the waste deposit area. Weirs placed at regular intervals along the ditch divert the solution to the spreading area. The direction of flow in the spreading area can be controlled by strategically placing embankments. Peripheral berms and a collection ditch at the lower end of the area are required to prevent the solution from flowing out of the application area. A typical plan of a ditch flooding system is shown on Figure 1-3. Information on construction parameters and costs of berm construction is presented in A D Little (1983).

Since the liquid is applied directly to the soil surface, even a thin layer of impermeable material between the surface and the waste deposit would impede infiltration of the liquid and make this application method ineffective. The natural infiltration rate can be enhanced by tilling or furrowing the surface

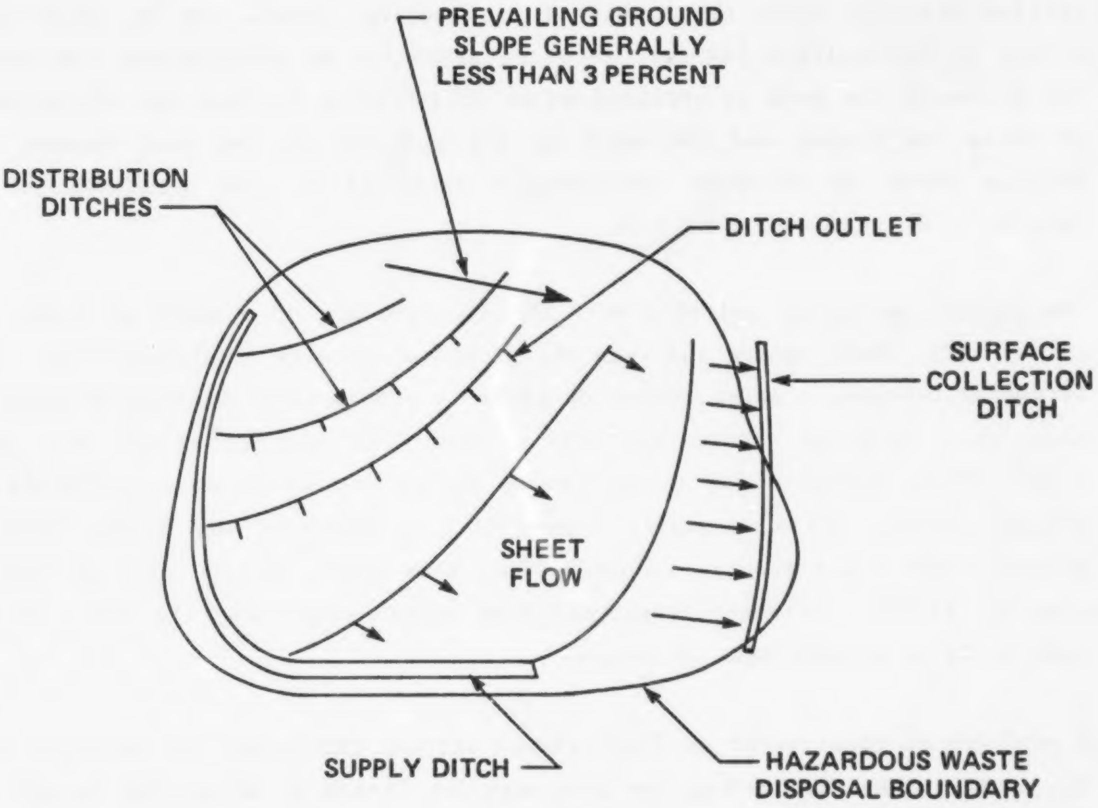
TABLE 1-2

DESIGN LIMITATION FOR INFILTRATION - PERCOLATION SYSTEMS

Factor	Range of Feasible Values
Liquid loading rate	10 to 300 cm/wk, or 2×10^{-5} to 6×10^{-4} cm/sec (4 to 120 in/wk)
Annual application rate	5 to 155 m/yr (17 to 500 ft/yr)
Land required for 1-mgd (3785 m^3/day)flow	1 to 25 hectares (2 to 62 acres) plus buffer zones
Application techniques	Usually surface
Soils	Rapidly permeable soils, such as sands, loamy sands and sandy loams

Source: Pound and Crites, 1973

FIGURE 1-3
TYPICAL PLAN OF DITCH AND FLOODING TYPE GRAVITY DELIVERY SYSTEM


PREVAILING GROUND SLOPE GENERALLY LESS THAN 3 PERCENT
DISTRIBUTION DITCHES
DITCH OUTLET
SURFACE COLLECTION DITCH
SHEET FLOW
SUPPLY DITCH
HAZARDOUS WASTE DISPOSAL BOUNDARY

soil (USEPA, 1977; USEPA, 1984b), but deeper impermeable layers may not be reached by this method and other delivery systems will therefore be required. Flooding should be implemented in a uniform manner so that dry spots do not result. Because the solution is applied in a thin sheet over the ground surface, it is susceptible to freezing, so this method is limited to use during non-freezing conditions. Also, because the solution is exposed to the atmosphere, this method is not suitable for application of reactants which are volatile or susceptible to photo-oxidation.

Ponding -- Ponding can be used to increase the infiltration rate of the applied solution above that achieved by flooding. Ponds can be constructed either by excavating a few feet into the ground or by constructing low berms. The bottom of the pond is utilized as an infiltrative surface for the solution to enter the ground and the depth of the solution in the pond becomes the driving force to increase infiltration rates (i.e., the gradient, I, in Equation 1-3 is greater than 1.0).

The ponding method is suitable when the deposits are of a sandy or loamy (SM or SW, ASTM, 1969) nature and when the ground surface is relatively flat. For irregular terrain, a large number of ponds or considerable excavation would be required. Although there is not a specified maximum slope for pond construction, constructing a pond would be progressively more difficult on steeper slopes. As an example, a pond with a length of 100 meters on a 10 percent slope would require a downgradient berm with a height greater than 10 meters. If 2:1 (horizontal:vertical) side slopes were used, the width of the base would be greater than 40 meters.

A pond can be constructed on level ground without excavating any material from the surface. By surrounding the area with low levees or berms, the liquid can be contained. In this manner, the contaminated area can be treated without having to remove any soil. Such a system is depicted on Figure 1-4. Information on construction costs of berms is presented in A D Little (1983). When the waste deposit is overlain by a relatively thin layer (less than 2 meters or 6 feet) of impervious material, the ponding method can be utilized by excavating the impervious layer. Figure 1-5 depicts such a system.

FIGURE 1-4
GRAVITY DELIVERY SYSTEM USING PONDING

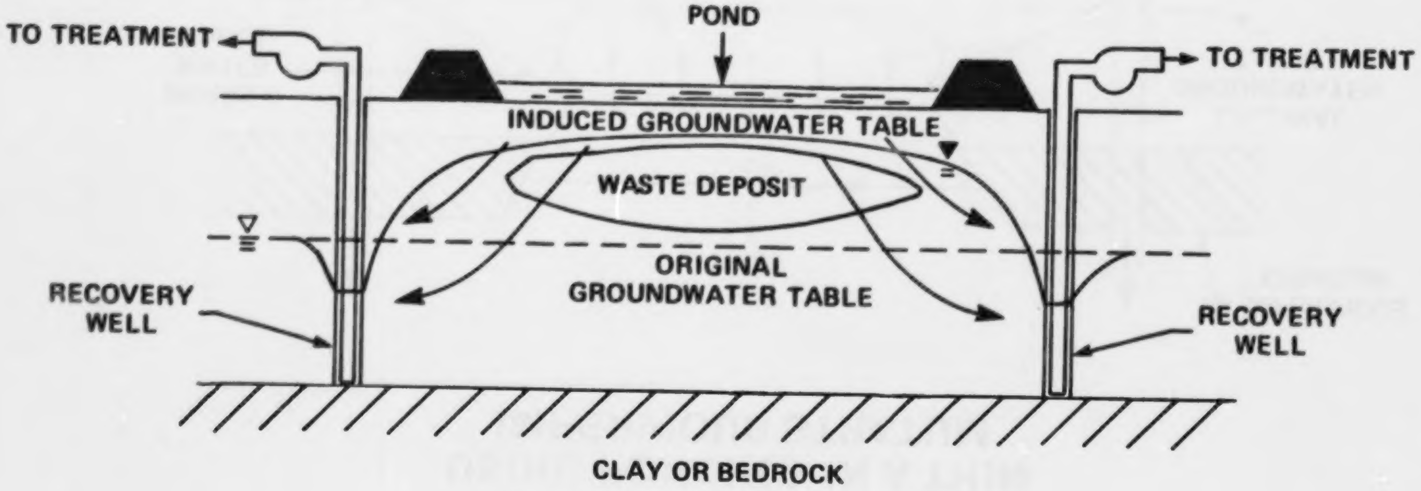
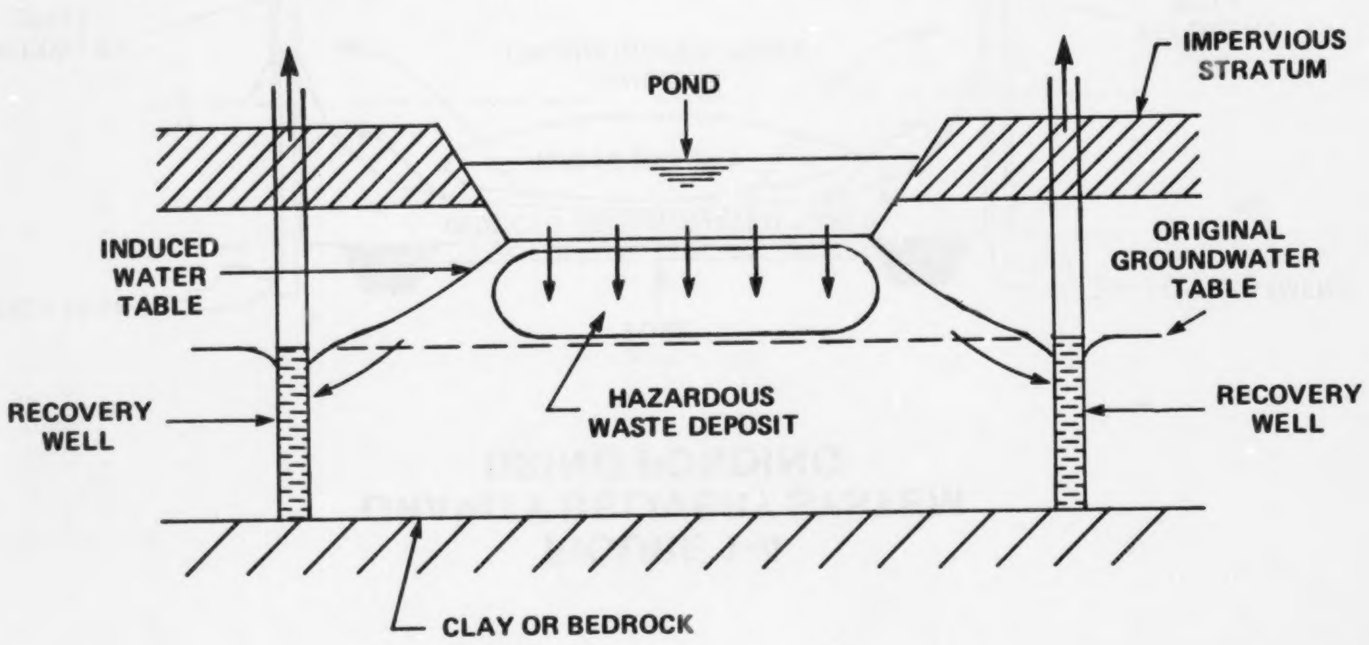

POND
TO TREATMENT
TO TREATMENT
INDUCED GROUNDWATER TABLE
WASTE DEPOSIT
ORIGINAL GROUNDWATER TABLE
RECOVERY WELL
RECOVERY WELL
CLAY OR BEDROCK

FIGURE 1-5
GRAVITY DELIVERY SYSTEM USING PONDING IN A THIN IMPERVIOUS STRATUM


POND
IMPERVIOUS STRATUM
INDUCED WATER TABLE
ORIGINAL GROUNDWATER TABLE
RECOVERY WELL
HAZARDOUS WASTE DEPOSIT
RECOVERY WELL
CLAY OR BEDROCK

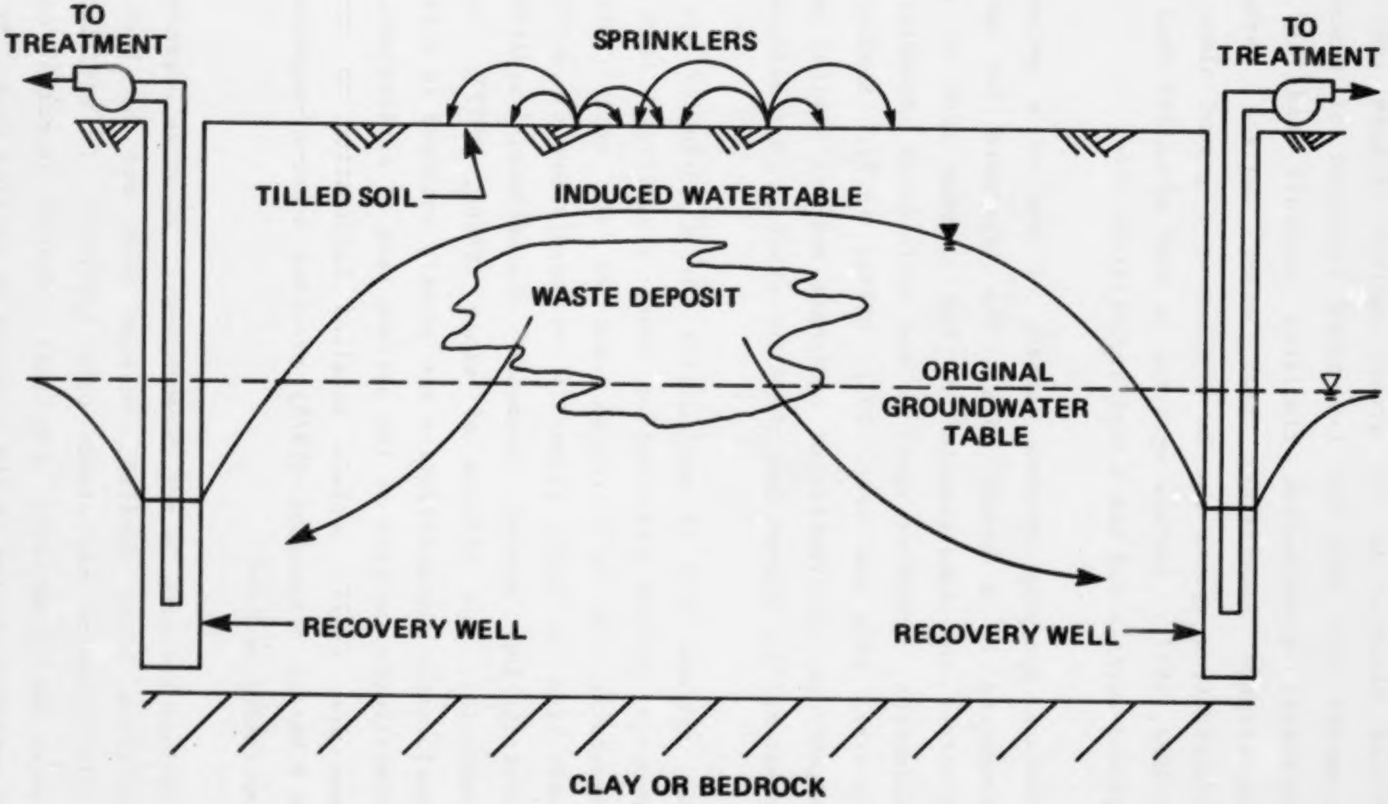
Surface Spraying -- Sprinkler-type irrigation systems are used to deliver the liquid directly to the ground surface (Figure 1-6). This technique has commonly been used for land-based treatment of wastewaters (USEPA, 1977). Sprinkler distribution simulates rainfall and is less susceptible to topographic constraints than other surface methods. The sprinkler distribution system can be applied on a ground slope of up to 20 percent (USEPA, 1977). Surface spraying is most effective when the deposit is at the ground surface and has a high infiltration rate.

Surface spraying systems consist of one or a series of sprinkler heads connected to a header pipe. The procedure for sprinkler system design involves the determination of the optimum rate of application, sprinkler selection, sprinkler spacings and performance characteristics, and design of laterals (Fry and Grey, 1971; USEPA, 1977). Surface spraying involves a significant utilization of equipment and its capital and operating costs are substantially higher than those for other gravity methods.

The optimum rate of application for a sprinkler system is the rate that ensures uniform distribution under prevailing climatic conditions without exceeding the infiltration rate of the soil (USEPA, 1977). Sprinkler selection is based primarily on conditions of service, such as type of distribution system, pressure limitations, application rate, clogging potential, and effects of winds (USEPA, 1977). Sprinkler spacings and performance characteristics are jointly analyzed to determine the most uniform distribution pattern at the optimum rate of application. USEPA (1977) and Fry and Grey (1971) contain detailed information on sprinkler system design. A W Martin Associates (1978) provides order-of-magnitude cost estimates for sprinkler systems.

Surface spraying is not recommended if volatile organics are contained in the solution being applied, because much may be lost by evaporation, and volatilization may create odor problems. In addition, photo-oxidation may occur during spraying operations. Another important consideration for use of a sprinkler system is the clogging of nozzles caused by scaling of the applied solution.

FIGURE 1-6
GRAVITY DELIVERY SYSTEM USING SURFACE SPRAYING


TO TREATMENT
SPRINKLERS
TO TREATMENT
TILLED SOIL
INDUCED WATERTABLE
WASTE DEPOSIT
ORIGINAL GROUNDWATER TABLE
RECOVERY WELL
RECOVERY WELL
CLAY OR BEDROCK

Ditches -- The ditch method of surface spreading utilizes relatively flat-bottomed ditches to transport the solution over the application surface providing the opportunity for percolation. Generally, ditches are relatively shallow and narrow (1 to 2 meters or 3-6 feet wide) and make use of both the bottom and side surfaces for infiltration of liquid to the ground. Gradients in the ditches should be slight for erosion prevention and maintenance of an adequate residence time for infiltration. Ditches can be constructed by excavating surface material or building small embankments. Figure 1-7 depicts a typical ditching system.

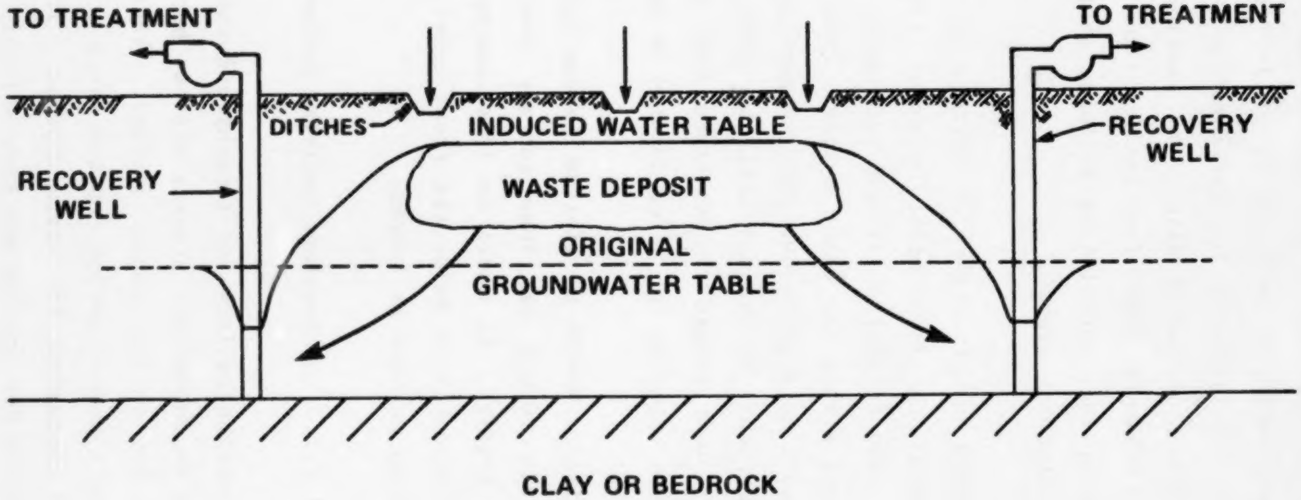
Ditches would be effective for surface application in circumstances where it is not desirable to completely cover the entire area with the reactant solution. Runoff control is not necessary, since all of the applied solution is contained within the ditch system. This method of application is suitable for a subsurface deposit overlain by pervious soils. If the surface layer is impermeable, this method may still be valid, providing that excavation of the ditches is deep enough to penetrate into more permeable materials. Ditches would not be suitable for sites located in areas of very irregular terrain.

Shallow ditches would be limited to use during non-freezing weather periods. Because this method has less surface area exposed to the atmosphere than flooding, however, it would be less susceptible to rapid freezing. If the floor of the ditch is below the frost level, infiltration can take place even if the ground surface is frozen.

1.2.1.5 Subsurface Delivery Systems

The infiltration gallery (or trench) and infiltration bed delivery methods are classified as subsurface gravity systems because the direct application of the liquid is not on the ground surface. These systems consist of excavations filled with a porous medium (coarse sands or gravels) that aid in distributing the liquid throughout the waste deposit. The large void spaces of the porous medium provide for storage and easy delivery of the solution.

FIGURE 1-7
GRAVITY DELIVERY SYSTEM
USING DITCHES


TO TREATMENT
TO TREATMENT
DITCHES
INDUCED WATER TABLE
RECOVERY WELL
RECOVERY WELL
WASTE DEPOSIT
ORIGINAL GROUNDWATER TABLE
CLAY OR BEDROCK

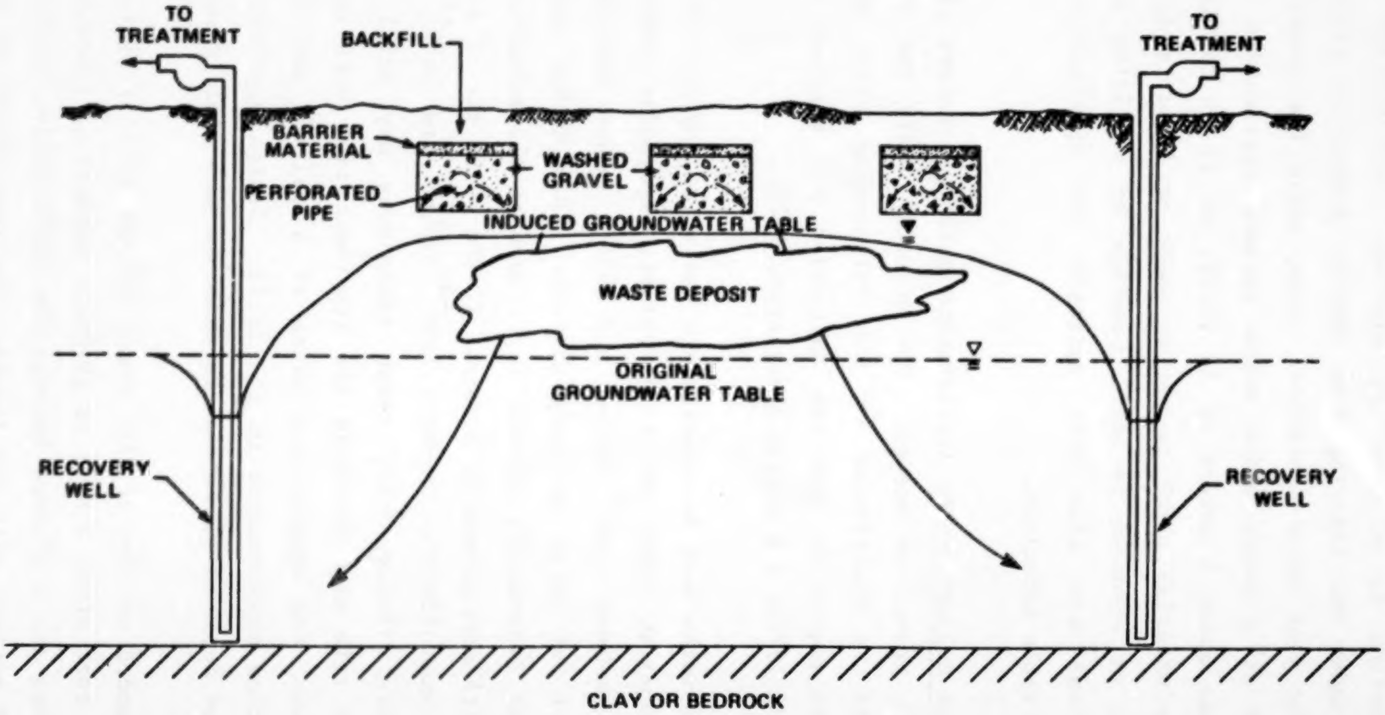
These methods are suitable where the waste deposit is subsurface and where ground freezing is a recurring problem. Infiltration galleries can be installed under the freezing zone thereby permitting gravity application of solution for year round operation. Also, where the subsurface waste deposit is located at a depth which makes surface application impractical (i.e., greater than about 5 meters or 16 feet), or it is overlain by a layer of impermeable material which is not economic or feasible to excavate, gravity application of solution is still possible by utilizing subsurface methods. These methods are also more suitable for application of volatile or photo-oxidizable materials.

Infiltration Gallery -- An infiltration gallery consists of a trench that is filled with gravel or stones. The solution fills the void spaces in the gallery and is distributed to the surrounding soils and waste deposit. Infiltration occurs in both the horizontal and vertical directions (Figure 1-8) (USEPA, 1980b; A W Martin Associates, 1978).

This method works best in cases where the waste deposit and surrounding soils are of a sandy or loamy (SM or SW) nature. Hydraulic conductivities of soils and wastes between $1x10^{-2}$ cm/sec and $1x10^{-4}$ cm/sec are (28 to 0.28 ft/day) best suited for these delivery systems. This method can be installed to penetrate an impermeable surface soil, so that the subsurface systems contact directly with more permeable strata. If the soils are of a silty nature, with hydraulic conductivities between $1x10^{-4}$ cm/sec and $1x10^{-5}$ cm/sec (0.28 and 0.028 ft/day) (Table 1-1), these techniques may still be used but the application rate and therefore the treatment time will be much slower. As with ditches, the application rates of a gallery are best determined by inflow-outflow measurements in the field. Design application rates, number, spacing, and depth of galleries are based on such field results.

The recommended packing of fill media for use in this system is either gravel or crushed rock sized 2 to 6 cm (0.8-2.5 inches) in diameter. Generally, the smaller sizes are preferred because the infiltrative surface of the soil has more direct contact with the liquid. The rock should be washed before being put in place to remove fines that may clog the bottom infiltrative surface.

FIGURE 1-8
SUBSURFACE GRAVITY DELIVERY SYSTEM USING INFILTRATION GALLERIES


TO TREATMENT
BACKFILL
TO TREATMENT
BARRIER MATERIAL
WASHED GRAVEL
PERFORATED PIPE
INDUCED GROUNDWATER TABLE
WASTE DEPOSIT
ORIGINAL GROUNDWATER TABLE
RECOVERY WELL
RECOVERY WELL
CLAY OR BEDROCK

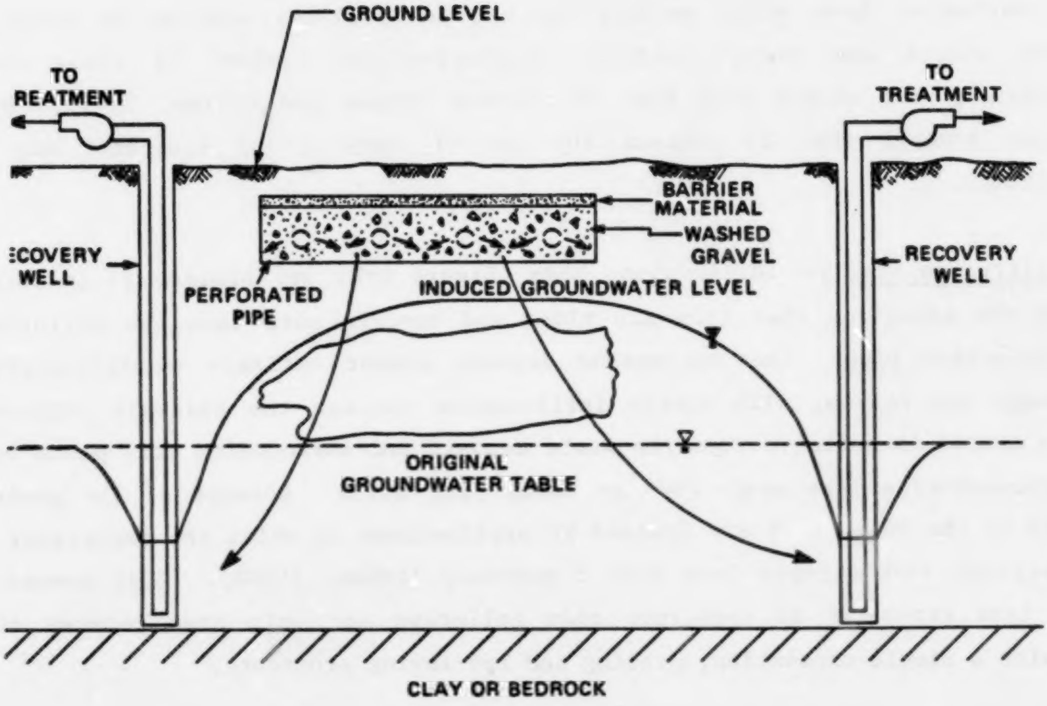
The solution can be introduced into the gallery by injection in different locations along the length of the gallery or through perforated distribution pipes. The pipe used for the distribution can be constructed of the following materials: clay, bituminized fiber, concrete, plastic (acrylonitrile-butadiene-styrene:ABS), polyvinyl chloride (PVC), styrene rubber plastic (SR), or polyethylene (PE). If water is to be the application liquid, then any of these materials will suffice. However, some of the plastic-type pipes may not be suitable for certain organics, bases, acids or other additives. This must be confirmed with the manufacturer before installation. The perforation size in the pipes, spacing of holes along the pipes and spacing between galleries will depend on site specific conditions (USEPA, 1980b).

Infiltration galleries provide effective gravity application methods in circumstances where other methods may not be feasible, such as in areas of steep slopes and uneven terrain. Galleries are limited to areas where topography has slopes less than 25 percent (Pound and Crites, 1973). With slopes steeper than 25 percent the use of construction equipment may be difficult.

Infiltration Beds -- Infiltration beds (Figure 1-9) are similar to galleries with the exception that they are wider and contain more than one perforated distribution pipe. The bed method depends almost entirely on infiltration through the bottom, with little infiltration through the sidewall surfaces. This method is suitable when the waste deposit and surrounding soil media have characteristics like sandy (SW) or loamy (SM) soils. Because of the greater width of the beds, they are limited to applications in which the topography is relatively flat (slopes less than 5 percent) (USEPA, 1980b). Beds generally are less expensive to construct than galleries per unit area because they require a single excavation, grading and bed-laying procedure.

Typically, the perforated distribution pipes within infiltration beds would be placed 1 to 2 meters (3-6 feet) apart. In cases of more impermeable soils, the pipe placement could be as close as 0.5 meters (1.5 feet). The design and the materials used for the bed system are similar to those for the gallery system.

FIGURE 1-9
SUBSURFACE GRAVITY DELIVERY USING INFILTRATION BED SYSTEM


GROUND LEVEL
TO
REATMENT
TO
TREATMENT
BARRIER
MATERIAL
WASHED
GRAVEL
ECOVERY
WELL
RECOVERY
WELL
PERFORATED
PIPE
INDUCED GROUNDWATER LEVEL
ORIGINAL
GROUNDWATER TABLE
CLAY OR BEDROCK

These systems would have the same limiting factors and effectiveness as infiltration gallery systems; however, infiltration bed systems are more limited by steep slopes and uneven terrain. Beds have the advantage of saturating a much larger area than a single trench. A bed is also simpler to install than a comparable multi-trench system, since the piping goes to a common header and the entire system is installed as one single excavation.

1.2.2 Forced Delivery Methods

Forced injection is the process in which a fluid under pressure is forced into the waste deposit and surrounding soil through pipes which have been strategically placed to deliver the solution to the zone requiring treatment. This method is generally suitable for a deposit having a hydraulic conductivity greater than $1x10^{-4}$ cm/sec (0.28 feet/day) which would represent a fine sand/coarse silt material.

The injection process may be accomplished by using either an open end or slotted pipe. An open end injection pipe as shown on Figure 1-10 consists of an EW size (3.5 cm or 1-3/8 inch OD) pipe or equivalent. The lower element of the pipe contains an expendable and movable point for driving into the ground without plugging. Additional lengths of pipe are added as it is driven to the desired depth. The slotted pipe (Figure 1-10) may be plastic (PVC) pipe, 3.8 cm (1.5 inch) in diameter placed in an 8 to 10 cm (3 to 4 inch) borehole. The lower portion of the pipe is slotted over an interval corresponding to the zone to be treated, and surrounded by gravel or coarse sand as shown on Figure 1-10. Above the slotted portion, a cement grout is placed around the pipe up to the ground surface. Figure 1-11 shows the application of injection wells in a waste deposit.

A forced delivery system, unlike the gravity systems, is conceptually independent of surface topography and climate and can be designed to accommodate any of the waste deposit configurations that have been discussed. Since the applicability and design of the forced injection delivery system depends heavily on the site geohydrological conditions, the site must be investigated by means of test borings with field hydraulic conductivity

FIGURE 1-10
INJECTION PIPES FOR FORCED DELIVERY

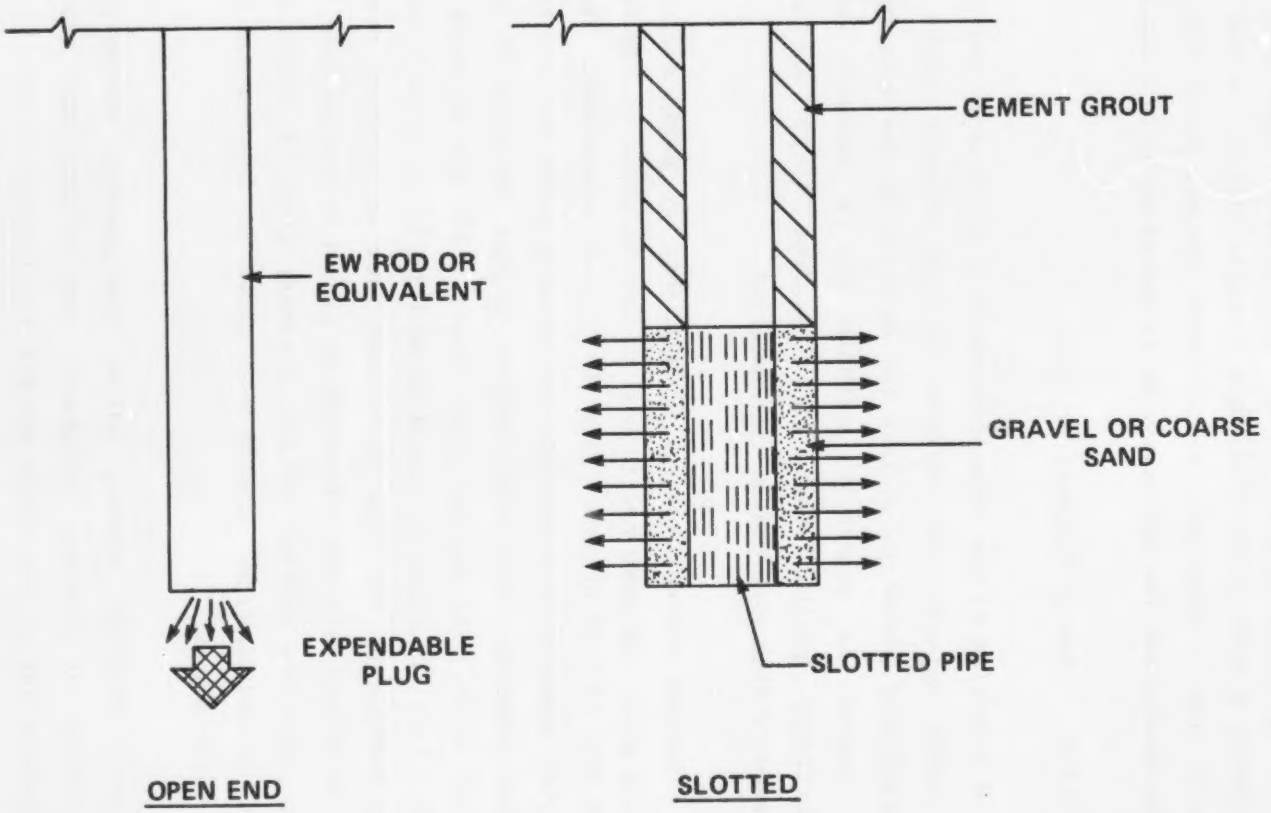
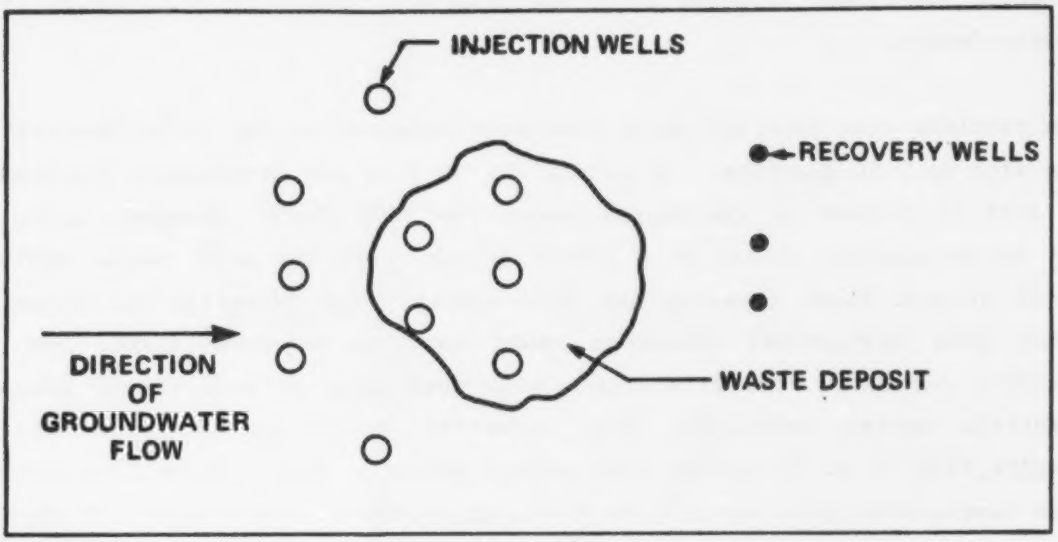
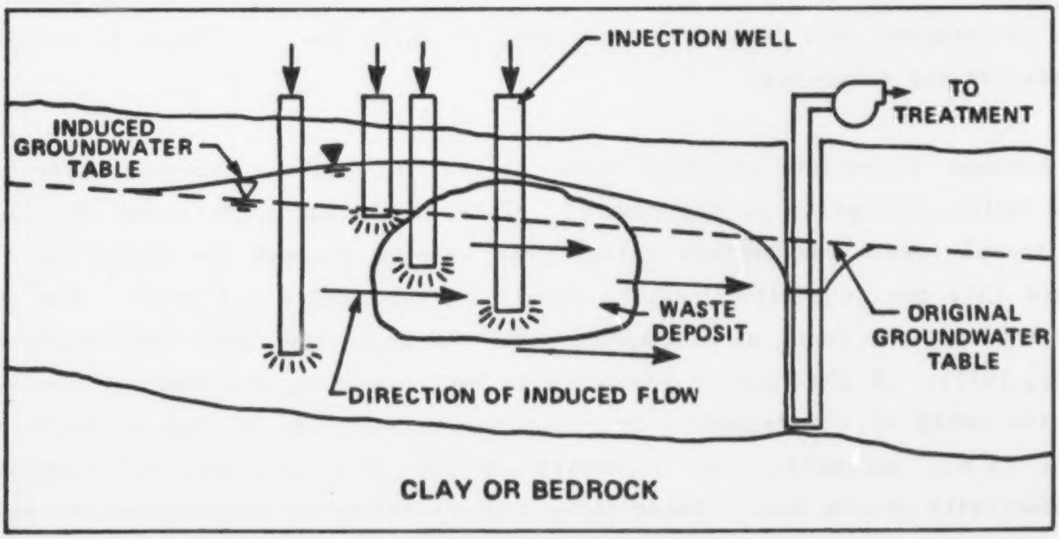

EW ROD OR EQUIVALENT
EXPENDABLE PLUG
OPEN END
CEMENT GROUT
GRAVEL OR COARSE SAND
SLOTTED PIPE
SLOTTED

FIGURE 1-11
FORCED DELIVERY USING INJECTION WELLS


INJECTION WELLS
RECOVERY WELLS
DIRECTION OF GROUNDWATER FLOW
WASTE DEPOSIT

PLAN VIEW


INJECTION WELL
TO TREATMENT
INDUCED GROUNDWATER TABLE
WASTE DEPOSIT
ORIGINAL GROUNDWATER TABLE
DIRECTION OF INDUCED FLOW
CLAY OR BEDROCK

CROSS SECTION

testing as well as laboratory geotechnical testing. Test borings serve primarily to establish or confirm the waste deposit configuration and the depth to the groundwater table, both of which will be essential in the layout of a forced injection system. In situ and laboratory tests can provide data on hydraulic conductivity, rates of groundwater flow and dispersion of injected solutions, particle size, and porosity, which are also needed for a system design.

The particle size analysis would give an indication of the "injectability" of the site soil in question. In general, a soil is not considered "injectable" if over 10 percent of the sample passes the #200 sieve. However, injection may be successful, albeit to a lesser degree, when the soil sample exhibits 10-20 percent fines (passing the #200 sieve). The potential for injection under this sub-optimal situation would have to be investigated for the specific deposit. Forced injection will work best in well-sorted granular materials having relatively high effective porosities (specific yields) ranging from 25 to 55 percent and average particle sizes larger than that of fine sand/coarse silt, about 0.05 to 0.1 mm (0.002 to 0.004 inch) (US Dept of Navy, 1982). In situ pumping tests can be made in exploratory borings to provide information on both the hydraulic conductivity and the flow rates under different injection pressures. The in situ hydraulic conductivity of the undisturbed soil determines the rates at which the fluid will be accepted under varying pressures.

A maximum injection pressure must be established to prevent hydraulic fracturing and uplift in the deposit. This fracturing might cause the fluid to travel toward the surface rather than seeping through the formation. To avoid this the injection pressure should be kept below 1.5×10^{-4} N/m^2 per meter (1 psi per foot) of overburden above the injection level (Winterkorn and Fang, 1975). If the rate of injection is kept constant, the pressure measured at the entry of the injection hole depends on the size of the voids in the soil (i.e., porosity), the viscosity of the solution, and the hydraulic conductivity of the soil. These three factors acting as resistances determine the relationship between pressure and rate of injection.

Depending on the injection pressure and the corresponding flow rate (Q) that is selected, a spacing between injection holes can be determined using the following formula (Huisman and Olsthoorn, 1983):

$$r = 0.62\ (Qt/n)^{1/3} \tag{1-13}$$

where:

r = radial distance of solution penetration (length)
Q = rate of solution application (length^3/time)
n = porosity of soil (dimensionless)
t = pumping time (time)

The pumping time (t) is determined by the configuration of the waste deposit and delivery/recovery system. It will be determined by dividing the measured flow rate (Q) by the theoretical distance traveled by an element of fluid from the injection point to the recovery point. This must all be within the time framework set up for the clean-up operation at the site. Based on the above equation, the well spacing should be approximately 2r. A grid work of injection wells would be set up accordingly, making sure to cover completely the contaminated area in plan.

It should be noted that open end pipes would be better suited for soils or waste deposits where it appears that the hydraulic conductivity in the vertical direction approaches the hydraulic conductivity in the horizontal direction (i.e., $K_v = K_h$). Slotted pipes, on the other hand, eject the solvent in the horizontal direction along the axis of the riser pipe. Therefore, they would be more useful in soils or waste piles where it appears that the horizontal hydraulic conductivity exceeds the vertical hydraulic conductivity (i.e., K_v is less than K_h).

1.2.3 Summary and Example Applications

As discussed in the foregoing sections, gravity and forced methods may be used for delivery of solutions to waste deposits. A number of gravity delivery methods including flooding, ponding, surface spraying, ditches, infiltration galleries and infiltration beds may be used. The selection of a particular gravity delivery method would depend upon: surface topography, infiltration rate, configuration of waste deposit, groundwater hydrology, hydraulic conductivity, soil porosity and local climate. Forced delivery would be cost-effective for a waste deposit and surrounding soil having a lower hydraulic conductivity (down to 1 x 10^{-4} cm/sec, or 0.28 ft/day) and low infiltration rate(below 10 cm or 4 inches per week), which would preclude the delivery of treatment solution by gravity. Such systems would typically be comprised of an injection pipe (open end or slotted) and pump. The applicability of any delivery system would depend heavily on the site geohydrological conditions. Test borings and in situ pumping tests should therefore be conducted prior to the engineering and design of the delivery system.

Determining the required application rate of treatment solution is the most important engineering effort for both gravity and forced delivery systems. The solution application rate must be established based on consideration of various site parameters and waste deposit characteristics as well as the location and rate of recovery system operation. An example is presented below to demonstrate the procedures to estimate the required/allowed application rate of treatment solution.

In this example, it is assumed that a field geohydrological survey was conducted and the following data were generated:

- The waste deposits lie immediately above the water table.
- The length (L) of the waste deposit parallel to the groundwater gradient is 30 m and its width is 40 m; i.e., area (A) = 1200 m^2.
- Height of the original water table above an impermeable layer (H_d) is 3 m.
- The thickness of the waste deposit is 1.5 m; thus the thickness of induced saturation (H_c) would need to be 1.5 m + H_d = 4.5 m.

- At the site, the surrounding soil is sandy with a hydraulic conductivity of 1×10^{-1} cm/sec.

- Field testing has shown that the sustained infiltration rate (I_s) is approximately 3.5×10^{-4} cm/sec and the soil porosity (n) is 45%.

- Laboratory geotechnical and waste tests have determined that the hydraulic conductivity of the waste deposit is approximately 1×10^{-1} cm/sec, and the reaction time (See Section 2-5) requires a maximum of 10 minutes.

The first step in establishing a delivery system concept is to determine the allowable application rate of solution based on the infiltration rate of the soil. Equation (1-12) is applied as follows:

$$Q_o = AI_s \tag{1-14}$$
$$= 1200 \times 3.5 \times 10^{-6} = 4.2 \times 10^{-3} m^3/sec = 0.25\ m^3/min, \text{ and}$$
$$q_o = Q_o/A = I_s = 2.1 \times 10^{-4}\ m^3 \text{ per square meter per minute.}$$

Thus, the maximum rate at which solution can be introduced into the soil is 0.25 m^3/minute, or 2.1×10^{-4} m^3 per square meter per minute.

The second step in the process is to determine the required application rate of solution based on the hydraulic conductivity and recovery system location (X). This application rate represents the flow required to maintain the in situ treatment system at steady state conditions, i.e., to maintain the waste deposit entirely under a saturated condition with a recovery system operated at a designated distance, and at a recovery rate equal to the delivery rate. The hydraulic conductivity of surrounding medium and waste deposit (K) is 0.06 m/minute. Equation (1-10) is then applied as follows:

$$q_1 = K(Hc^2-Hd^2)/L(L+2X)$$
$$= 0.06\ (4.5^2-3^2)/30\ (30 + 2X)$$
$$q_1 = 0.68/(900 + 60X)$$

The third step in the process of establishing the conceptual design is to set $q_1 = q_o$ to define the minimum distance the recovery system should be located from the edge of waste deposit (X_{min}). Setting q_1 equal to 2.1×10^{-4} m/min (from above) and solving for X, one obtains $X_{min} = 39$ m, which can be rounded to 40 m.

The fourth step is to determine the time required to saturate the waste deposit and surrounding soil prior to the commencement of steady state operation. Equation (1-11) is applied for this purpose as follows:

$$t = \frac{n(H_c - H_d)X}{2qW}$$

$$t = \frac{0.45\ (4.5 + 3) \times 40}{80q} = \frac{1.69}{q} \qquad (1\text{-}11)$$

If the actual application rate $q = q_o = q_1$, t = 8036 min = 5.6 days. It appears that the duration of approximately 6 days to saturate the waste deposit completely and to start the recovering operation is reasonable. Based on t = 6 days, the initial application rate will be 0.27 m^3/min. Thereafter, operated at 0.27 m^3/min (71 gpm) the delivery/recovery system would be at steady state.

Another illustration for consideration is an area of clayey soil with a waste deposit that has a low permeability similar to the surrounding clay medium. Presented below are the basic assumptions for this example.

$H_c = 4.5$ m
$H_d = 3$ m
$K = 1 \times 10^{-4}$ cm/sec $= 6 \times 10^{-5}$ m/minute
$L = 30$ m
(Waste Deposit Area (A) = L x W = 30 x 40 m^2 = 1200 m^2
$n = 0.3$ (30%)
$I_s = 7 \times 10^{-5}$ cm/sec

Determining q_o and q_1 yields:

$$q_o = 7 \times 10^{-5} \text{ cm/sec} = 4.2 \times 10^{-5} \text{ m}^3\text{/square meter per minute}$$
$$q_1 = 6 \times 10^{-5} (4.5^2 - 3^2)/30\ (30 + 2X)$$
$$= 6.8 \times 10^{-4}/(900 + 60X)$$

Letting $q_o = q_1$ results in $X = -14.7$ m. A negative solution indicates that the soil hydraulic conductivity (as reflected by q_1) rather than infiltration (as reflected by q_o) governs the application process. Thus, a solution for this situation can be achieved only by assuming the location of a recovery system, calculating the saturation (q_1) value, checking that it is less than q_o, then checking this against q and t estimated for the site.

As an example, assume a reasonable distance of 25 m for the location of the recovery system downgradient of the waste deposit. Then,

$$q_1 = 3.8 \times 10^{-6} \text{ m/minute}$$
$$t = 0.30\ (4.5 + 3)\ 25/80q$$
$$= 0.70/q$$

Letting $q = q_1$, $t = 1.9 \times 10^5$ min = 128 days.

The practical application flow rate (Equation 1-12) will be:

$$Q_o = q_1 A = 3.8 \times 10^{-6} \times 1200 = 4.6 \times 10^{-3} \text{ m}^3\text{/min (1.2 gpm)}$$

Delivering an approximate flow of 4 liters per minute over an area of 1200 m^2 is not considered a reasonable practice. Similarly, a saturation time of over 3 months may be considered unreasonable. Therefore, a forced method should be applied instead of a gravity delivery method.

1.3 Recovery Technologies

The available recovery technologies can, like delivery technologies, be grouped into two general categories: gravity and forced methods. The recovery technologies discussed herein for in situ treatment of waste deposits are those widely used in groundwater recovery and construction dewatering operations. Gravity recovery depends upon interception of the groundwater downgradient from the waste deposit (i.e., down the regional groundwater gradient or radially in the case of an induced groundwater mound). Thus, after applied treatment solutions pass through the waste deposit and enter the groundwater, the resultant fluid is collected in an interceptor system (i.e., open ditch or buried drain) by simple gravity flow. Forced recovery systems utilize well points, deep wells or vacuum well points located downgradient of (or radial to) the waste deposit to remove spent solutions by mechanical means. The primary factors affecting the application of recovery methods are: depth to groundwater, depth to impermeable layer, and geohydrologic properties of the waste deposit and surrounding soil.

Depth to groundwater is a constraint for gravity systems only to the extent that there are practical limits to which excavation can be performed (typically less than 5 meters or 16 feet: Huisman, 1972) before costs become excessive or related widths of excavation become impractical. For forced systems, depth to groundwater affects system installation costs and operational energy consumption costs. Depth of the water table aquifer (i.e., depth to impermeable layer) is a constraint on gravity systems and wellpoints because it is sometimes necessary (depending on waste and local geohydrologic conditions) for the recovery system to penetrate much of the thickness of the aquifer to ensure complete recovery. Thus the operation limits of gravity systems and wellpoints may preclude the use of these systems in such circumstances.

The primary geohydrologic property affecting recovery system application and feasibility is hydraulic conductivity. As hydraulic conductivity is reduced, the rate of spent solution recovery is decreased, thus increasing the period necessary for recovery. In a related manner, forced recovery systems will require greater energy utilization as hydraulic conductivity decreases. Hydraulic conductivity is related to the grain size distribution within the waste deposit and soil. Table 1-1 depicts the general relationship between hydraulic conductivity and effective grain size (D_{10}) distribution of a soil with water as the transported fluid (Federal Highway Administration, 1976). For any recovery system being considered, the groundwater flow to the system should be determined using conventional hydrologic analyses or mathematical modeling. Hydrologic analysis of flow to recovery systems is covered in Freeze and Cherry (1979), Cedergren (1981), Bouwer (1978) and Federal Highway Administration (1976). Repa and Kufs (1985) provide a good practical handbook on groundwater recovery.

1.3.1 Gravity Recovery Methods

Gravity recovery of spent solution and reaction products from a waste deposit can be accomplished through the use of open ditches or buried perforated pipes. The flow to the gravity recovery system is governed by the same factors that control flow to a well (e.g., hydraulic conductivity and hydraulic gradient), in accordance with Darcy's Law (Equation 1-3). Whereas hydraulic conductivity is a function of the waste deposit and surrounding soil, hydraulic gradient can be controlled by appropriate placement of the gravity recovery system in relation to the waste deposit and groundwater table. However, since the objective of the delivery system is to maintain saturation throughout the depth of the deposit, attention must be given to assure that saturation occurs. Bouwer (as presented in USEPA, 1977) has developed an equation to determine the distance at which recovery systems should be placed. This is the same equation introduced in Section 1.2.1 where the recovery distance (X) from the outer edge of the infiltration area (see Figure 1-12) can be calculated as:

$$X = K\,(H_c^2 - H_d^2)\,/\,2q\,L - L/2 \qquad (1\text{-}15)$$

where: K = Hydraulic Conductivity (length/time)

q_1 = Solution application rate/unit area of the deposit (length/time)

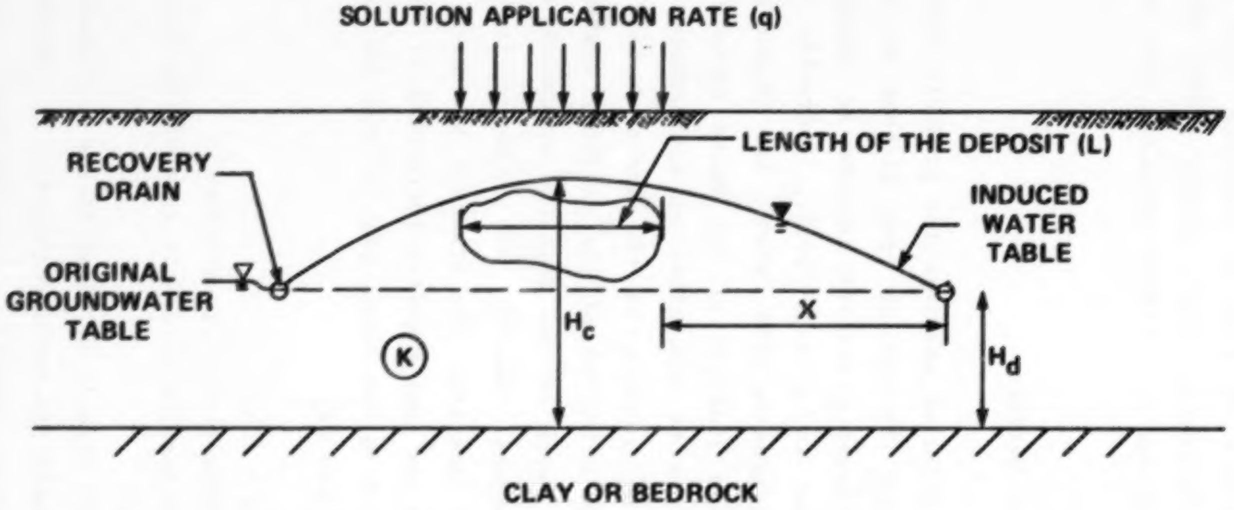
L = Length of the deposit parallel to the groundwater flow, (length)

H_c = Total saturated thickness required, i.e., distance from the top of the waste deposit to the impermeable layer (length)

H_d = Height of the recovery system above impermeable layer (length)

FIGURE 1-12

METHOD FOR CALCULATING LOCATION OF A BURIED PIPE RECOVERY SYSTEM


SOLUTION APPLICATION RATE (q)
LENGTH OF THE DEPOSIT (L)
RECOVERY DRAIN
INDUCED WATER TABLE
ORIGINAL GROUNDWATER TABLE
X
H_c
H_d
K
CLAY OR BEDROCK

1) RECOVERY DISTANCE (X) = $(H_c^2 - H_d^2)K/2q - L/2$

2) MAXIMUM GRAVITY APPLICATION RATE (q_o) = LI

(I = NATURAL INFILTRATION RATE)

SET $q = q_o$ TO DEFINE MINIMUM X

IF X IS TOO LARGE FOR THE SITE, THEN:

- INCREASE q_o (INCREASE HYDROSTATIC HEAD; TILL SURFACE)
- USE FORCED DELIVERY SYSTEM

Therefore, X can be determined by measuring K and setting H_d, measuring the depth of the deposit, and using the q_1 value determined for the delivery system.

1.3.1.1 Open Ditch

Open ditches, consisting simply of a ditch or trench excavated into the groundwater table, have been used successfully for the collection and transport of groundwater from shallow aquifers. The recovered liquid is ultimately conveyed to a sump from which it can be either returned to the delivery system, collected for disposal or further treated. The ditch may or may not be lined with stones or some other porous medium to maintain the structural stability of the side slopes. Ditches and trenches work best in permeable media such as sands, where the hydraulic conductivity is greater than 1×10^{-3} cm/sec (2.8 ft/day).

Generally, open ditches are limited to depths not exceeding 4-5 meters (13 to 16 feet) below ground level and the absolute maximum that has been recommended for groundwater recovery is approximately 8 meters (25 feet) (Federal Highway Administration, 1976). Since the recommended side slopes are usually within the range of 1:1.5 to 1:2 (vertical:horizontal), a ditch 8 meters (25 feet) in depth could have a width at the surface of more than 32 meters (100 feet). Clearly, the surface expression of deep trenches becomes quite large and volumes of earth to be removed become significant. A further consideration is that since they are open to rainfall, ditches that are deep and have side slopes of 1:2 or greater may take in considerable amounts of direct rainfall. If the ditches lead to a treatment system, this will put an additional load on that system.

Ditches can be installed on moderately steep terrain (slopes less than 25 percent). For steeper slopes, the upgradient end of the excavation would become progressively more extensive, thus increasing trench excavation volume. Also, problems may be encountered in mobilizing excavation equipment on very steep slopes.

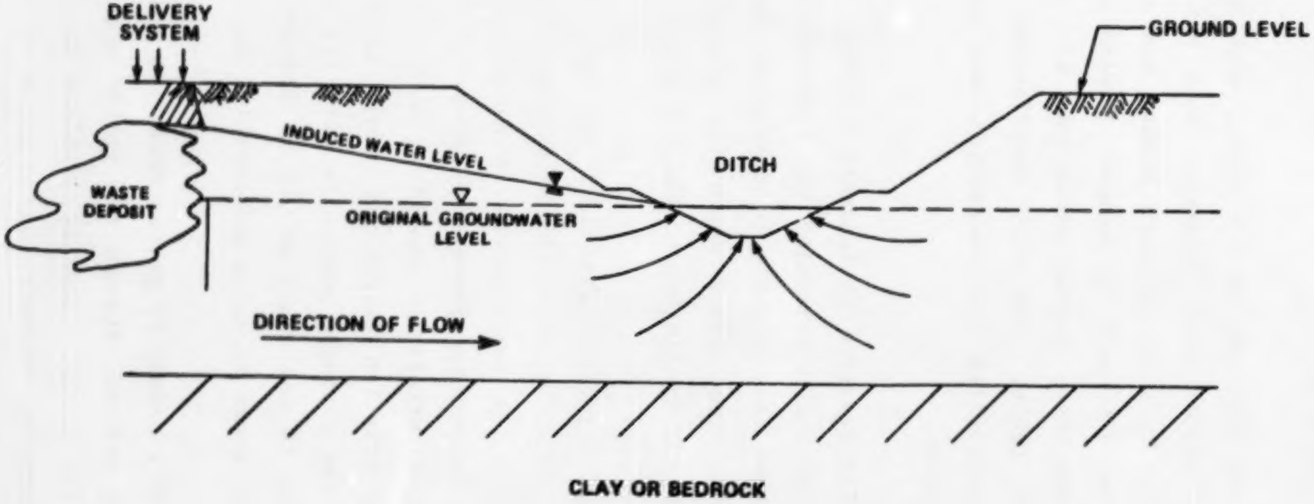
Ditches should be designed to a minimum depth of 1-1.5 meters (3 to 5 feet) below the groundwater table. Upon selection of the drainage ditch, the depth from the bottom of the ditch to the impervious layer beneath the water table aquifer (H_d) should be determined and groundwater flow from the infiltration area to the recovery ditch should be modeled to ensure that the ditch will recover all of the applied solution. If not, then the design of the ditch (both horizontal and vertical extent) should be altered to assure that the recovery will be complete and that the waste deposit remains saturated.

The design of recovery ditches is described in Federal Highway Administration (1976) and order-of-magnitude construction costs are presented in A D Little (1983). A typical design is shown in Figure 1-13. Because ditches and trenches are designed to transport the spent solution in addition to recovering it, they should be designed with a cross section of adequate area and relatively gentle slope (1 to 5 percent) to control water velocities, reducing friction losses and erosion of the side slopes. For unconsolidated deposits, the velocity in the ditches or trenches must be kept well below the scour velocity. A porous (gravel fill) lining can be added to prevent erosion if higher velocities are desired or required.

1.3.1.2 Buried Drains

Buried drainage pipes containing either slots, perforations, or open joints are another type of gravity collection method similar to the infiltration galleries described in Section 1.2.1 (gravity delivery techniques). The drainage systems are constructed by excavating a trench and laying drainage pipes, made of steel, concrete, asbestos-cement, clay, or plastic, at the bottom. The trench is then backfilled with gravel or other porous material to a designated depth (up to the saturated water level) and the rest of the trench is backfilled with soil. Often the gravel is covered with fabric to prevent fine soil from entering the gravel from above and clogging the drain. An impermeable barrier (liner or slurry trench) may be required on the down-gradient end of the trench to prevent the flowthrough of the intercepted and contaminated groundwater if the surrounding materials have a moderately high permeability. Detailed information on drain construction is provided in

FIGURE 1-13
GRAVITY RECOVERY USING A DITCH


DELIVERY SYSTEM
GROUND LEVEL
INDUCED WATER LEVEL
DITCH
WASTE DEPOSIT
ORIGINAL GROUNDWATER LEVEL
DIRECTION OF FLOW
CLAY OR BEDROCK

Federal Highway Administration (1976), Luthin (1957), U S Dept of Agriculture (1972), and Repa and Kufs (1985). A buried drain collection system is illustrated on Figure 1-14.

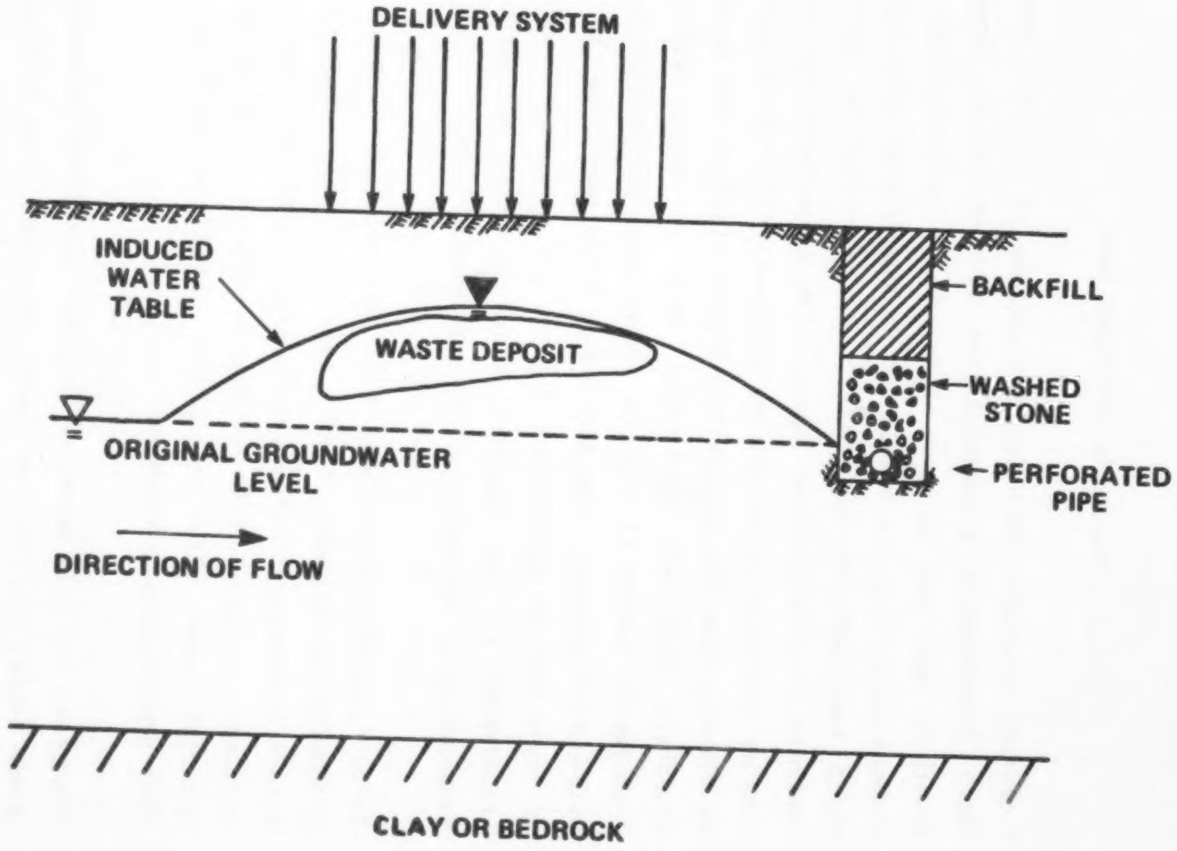
Buried drains are best suited for sands, with hydraulic conductivity greater than 1.0×10^{-3} cm/sec (2.8 ft/day). They can be utilized in silty soils but will result in long recovery times, and complete recovery of applied solutions may be difficult to ensure. Drains can be installed in areas of rough terrain and steep slopes, since they will be completely embedded within the groundwater table. The only restrictions on the installation of the drains is accessibility for excavation and pipe laying equipment to the particular location.

It is technically feasible to excavate a trench to almost any depth desired; however, the cost of construction could become prohibitively high. Although hydraulic backhoes can excavate to depths of about 15 meters (50 feet), for economic reasons, the trench depth for groundwater recovery from a waste disposal site should be limited to about 5 meters (16 feet) below ground level.

The same design principle discussed for open ditches will also apply for buried drains. The location (both horizontal and vertical) should be such that it satisfies the requirements in Equation (1-14). The velocity in the pipe should be maintained above 0.5 meters (1.5 feet) per second to prevent settling of any materials and should be less than 1 meter (3 feet) per second to prevent high friction losses and uneven distribution of the drawdown over the length of the drainage pipe. As with all delivery or recovery systems, groundwater flow to the drain should be modeled to determine that the drain will recover the spent solution and reaction products.

The disturbed area caused by porous drains is relatively small compared with a trench or ditch system. Because the drains are placed within the water table and covered with earth, freezing problems do not occur during the winter months. Furthermore, recovery of volatile or photo-oxidizable compounds is enhanced. Porous drains can clog because of chemical precipitates, and this may require an extensive maintenance effort to correct. The expense of

FIGURE 1-14
GRAVITY RECOVERY WITH BURIED PIPES


DELIVERY SYSTEM
INDUCED WATER TABLE
WASTE DEPOSIT
BACKFILL
WASHED STONE
PERFORATED PIPE
ORIGINAL GROUNDWATER LEVEL
DIRECTION OF FLOW
CLAY OR BEDROCK

installing a porous recovery drain is high, and the volume of groundwater recovered by this gravity system is low compared to pumping methods, although operating costs are much lower (Federal Highway Administration, 1976; A W Martin Associates, 1978; A D Little, 1983).

1.3.1.3 Permeable Treatment Beds

Permeable treatment beds are a variation of recovery trenches or drains, in which contaminated groundwater is treated as it flows through the bed. Treatment beds may be used alone if the contamination is primarily in the aqueous phase (e.g., a spill), or in combination with other treatment methods which remediate the contaminant source while the permeable treatment bed controls the downgradient plume. The groundwater may then be recovered for further treatment or discharge; alternatively, the treated groundwater may not be removed from the ground but simply continue its natural flow. Permeable treatment beds are applicable only to sites with relatively shallow groundwater tables (i.e., the limitations are similar to those for recovery with buried drains). The bed should fully penetrate the contaminant plume and be keyed into an impermeable stratum for maximum exposure of the contaminated groundwater to the treatment material (this is particularly true if the groundwater is not subsequently recovered).

To date, permeable treatment beds have not been used for in situ treatment of contaminants, although bench- and pilot-scale tests have been performed to determine treatment effectiveness (Park, 1985; Repa and Kufs, 1985). Potential problems in using this technique include chemical saturation of the bed material, short effective life of the bed material and plugging of the bed with precipitated substances.

Potential bed fill material includes limestone, activated carbon, glauconitic green sands, coal, fly ash, soil containing clay materials, natural (zeolites) or synthetic ion exchange resins, and polymeric adsorbents (Park, 1985; Repa and Kufs, 1985). Limestone would be used primarily for neutralization of acids or precipitation of metals. However, the increase in groundwater pH as it passes through a limestone bed may increase the rates of base-catalyzed hydrolysis of some organic contaminants in the groundwater (see Section 5.0). Activated carbon is commonly used as a treatment method for adsorption of hydrophobic (non-polar) organic contaminants in water. However, significant problems such as plugging of the bed, short lifetime or saturation of the carbon, and desorption might occur with the use of activated carbon in permeable treatment beds (Repa and Kufs, 1985). Glauconitic green sands are used primarily to treat trace metal contamination. Reduction of odors (Spoljaric and Crawford, 1978; as cited by Repa and Kufs, 1985) during treatment with this material suggests that volatile organic compounds may also be adsorbed. Coal and fly ash appear promising for adsorption of organics (Park, 1985), but leaching of other contaminants (e.g., trace metals) needs to be evaluated. Zeolites and ion-exchange resins are used primarily for adsorption of trace metals, but synthetic polymeric adsorbents (macroreticular resins, e.g., XAD resins) effectively adsorb a wide range of organic compounds. The high cost of these resins, however, would severly limit their use in situ unless a built-in regeneration system were included in the design.

In summary, permeable treatment beds may have limited application in specific cases, particularly for temporary remedial measures, but their costs and limitations render their use for long term in situ treatment of organic contaminants unlikely at present.

1.3.2 Forced Recovery Methods

Forced recovery is the process by which a fluid is pumped from pipes or wells strategically placed in the waste deposit for removal, recycle or treatment. When employed in shallow groundwater regimes, such systems are called wellpoint systems. When employed in deep groundwater regimes, such systems are termed deep well systems. The design rate of removal of liquid from the wells should be greater than the rate that the reactant solution is being delivered (by gravity application or injection), since some surrounding groundwater will also be drawn into the recovery system. The specific recovery rate required will depend on hydrologic conditions at the site, and should be determined by modeling the groundwater flow regime from the point of delivery to the recovery system.

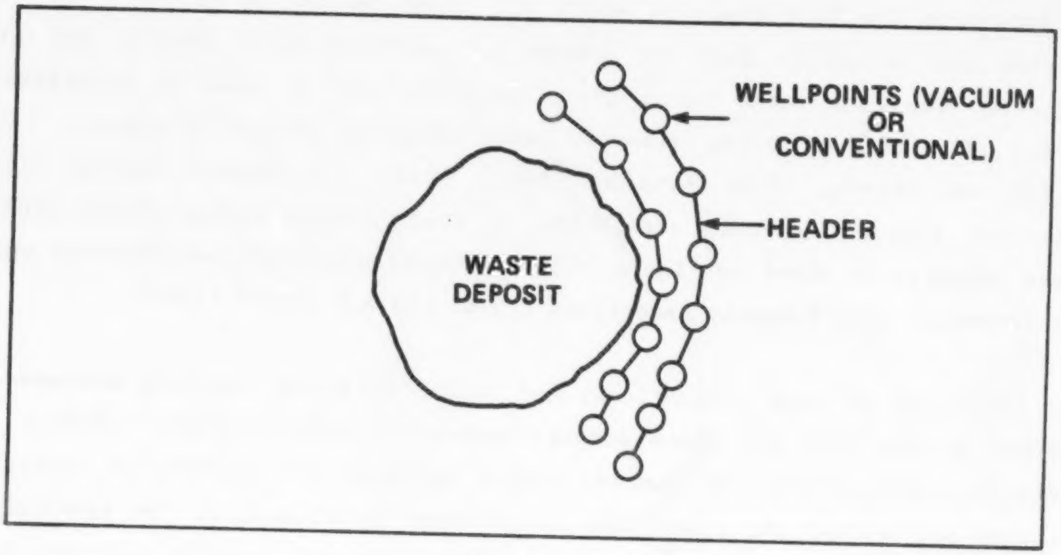
1.3.2.1 Wellpoint Systems

Wellpoint systems are the most commonly used dewatering methods in construction practice today and such systems are applicable to a wide range of excavations and groundwater conditions. The technology can be readily adapted for use as a recovery system in managing waste deposits. A wellpoint system is usually the most practical method for dewatering where the site is accessible, the groundwater is shallow and hydraulic conductivity of the waste deposit and surrounding soil media ranges between $1x10^{-1}$ and $1x10^{-3}$ cm/sec (280 to 2.8 ft/day). For deep groundwater conditions, more than about 8 meters (25 feet), it will be necessary to use ejector wells (Repa and Kufs, 1985) or deep wells with turbine or submersible pumps.

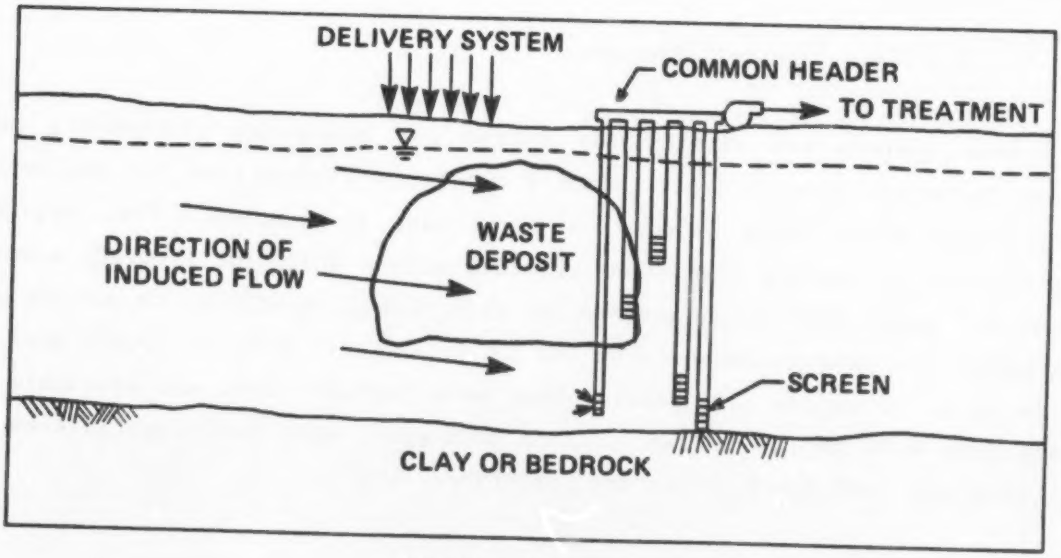
A conventional wellpoint system consists of one or more stages of wellpoints (wellpoints connected to a header at a common elevation) which are installed in a line, a ring or radially around the waste deposit at spacings of from 1-5 meters (3 to 15 feet). The wellpoints are attached to 3.8 or 5 cm (1 1/2 or 2 inch) riser pipes connected to a common header pumped with one or more wellpoint pumps as shown on Figure 1-15. The wellpoints are small well screens composed of either brass or stainless steel mesh, slotted brass or plastic pipe, or wire wrapped on rods to form a screen. Wellpoints generally range in size from 5 to 10 cm (2 to 4 inches) in diameter and 1 to 1.5 meters (3 to 5 feet) in length, and are constructed with either closed ends or self-jetting tips. It may be judged necessary to add a filter around the wellpoint, depending upon the nature of the waste deposit area being drained. A wellpoint pump is a combined vacuum and centrifugal pump which is connected to the header and pumps water from the wellpoints. Generally, a stage of wellpoints would be capable of draining a deposit about 5 meters (16 feet) thick. Draining a deposit that is greater than 5 meters (16 ft) thick generally requires a multi-stage installation of wellpoints.

A vacuum wellpoint system is essentially the same as a conventional wellpoint system except that a partial vacuum is maintained in the sand filter around the wellpoint and riser pipe. This vacuum increases the hydraulic gradient

FIGURE 1-15
WELLPOINT SYSTEM FOR FORCED RECOVERY


WELLPOINTS (VACUUM OR CONVENTIONAL)
HEADER
WASTE DEPOSIT

PLAN VIEW


DELIVERY SYSTEM
COMMON HEADER
TO TREATMENT
WASTE DEPOSIT
DIRECTION OF INDUCED FLOW
SCREEN
CLAY OR BEDROCK

CROSS SECTION

producing larger flows to the wellpoints (Fruco and Associates, 1966). Vacuum wellpoint systems are used in deposits with hydraulic conductivities from $1x10^{-3}$ to as low as $1x10^{-5}$ cm/sec (2.8 to 0.03 ft/day).

Actual field pump testing at the desired recovery elevation must be performed to determine the flow rates at which the fluid can be recovered. This will provide the necessary data to design the recovery well spacing and grid pattern. The flow rates for a given wellpoint can be used to calculate a radius of drawdown, using standard well drawdown theory (Urguhart, 1968; Freeze and Cherry, 1979; Repa and Kufs, 1985). A typical layout for a wellpoint recovery system, consisting of installations downgradient from a waste deposit, is shown on Figure 1-15. Order-of-magnitude construction costs are presented in A W Martin Associates (1978) and A D Little (1983).

The efficiency of both conventional and vacuum wellpoint recovery systems are limited by the soil and waste deposit hydraulic conductivities. With a low hydraulic conductivity, the pumping period required for recovery of treatment solution may exceed the time frame established to accomplish the remediation of the waste deposit. Under these conditions, the well spacing may also have to be very close, resulting in an unacceptable capital and operating cost.

1.3.2.2 Deep Well Systems

Deep well systems are particularly suited for recovering groundwater from depths below the suction limit (about 8 meters or 25 feet) or for dewatering large areas where large volumes of fluid must be removed. This requires higher rates of pumping than those obtained with a wellpoint recovery system. Mixed and axial flow pumps powered by electricity, gasoline, or diesel are available in discharge ranges from 0.3 to 1.6 m^3/sec (5000 to 25,000 gpm) at heads up to 30 meters (100 feet). Deep well turbine pumps are available in sizes from 0.01 to 0.4 m^3/sec (200 to 6000 gpm), with head capabilities up to 180 meters (600 feet) (Fruco and Associates, 1966).

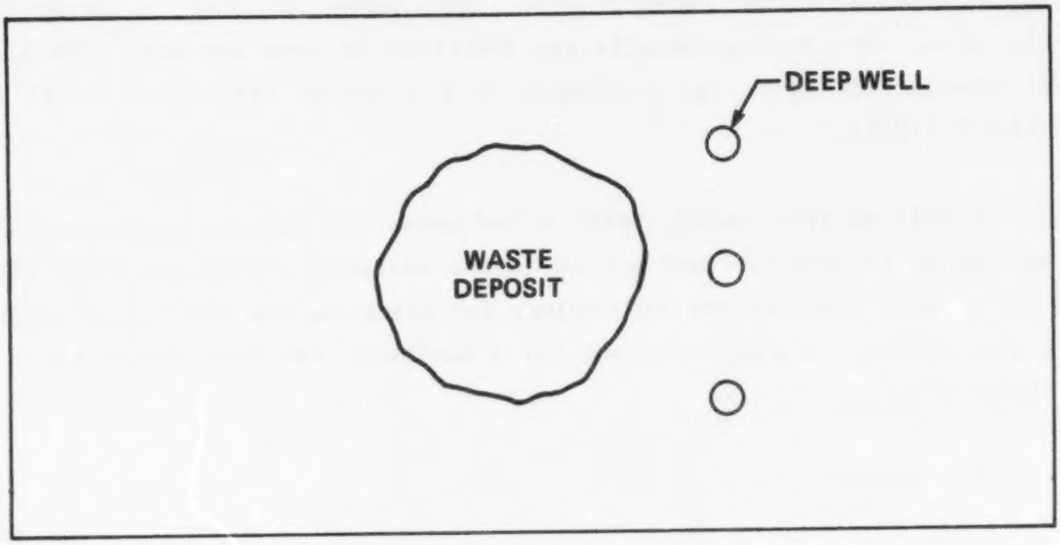
Deep wells for dewatering are similiar in type and construction to commercial water wells. They commonly have screens with a diameter of 10 to 45 cm (4 to 18 inches) and lengths up to 90 meters (300 feet). A filter is usually installed around the screen to prevent the infiltration of the deposit materials into the well and to improve the yield of the well. As in the case of a wellpoint system, deep wells may also be used in conjunction with a vacuum established at the recovery area. This serves to induce a larger flow to the well. Construction details are described in Repa and Kufs (1985) and order-of-magnitude costs are estimated in A W Martin Associates (1978) and A D Little (1983).

Actual in situ recovery rates, radii of influence and spacing arrangement will be arrived at in much the same way as in the wellpoint recovery systems (Repa and Kufs, 1985, describe the methodology for assessing the effects of pumping from deep wells). A typical layout for a deep well recovery system is shown on Figure 1-16.

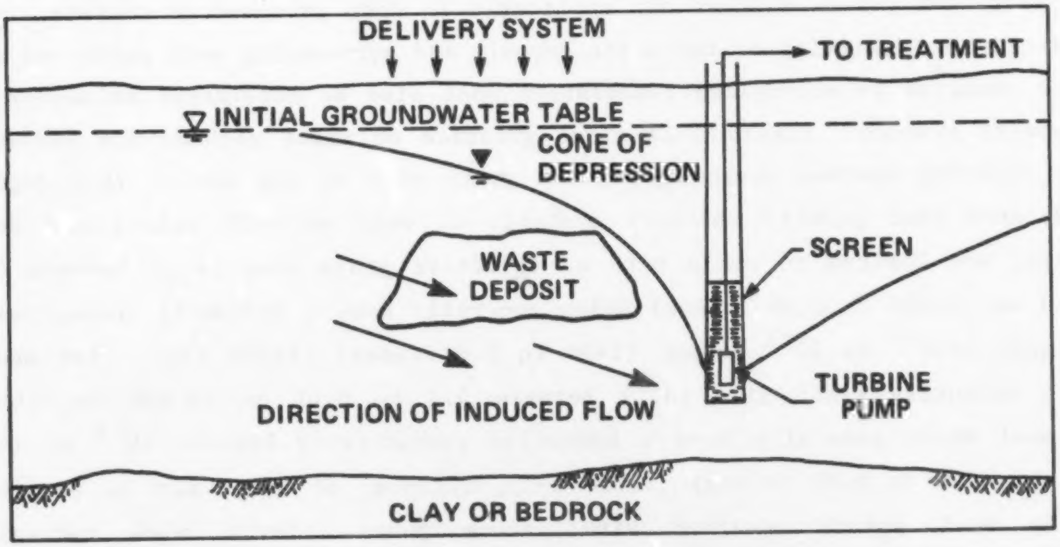
1.3.3 Summary

Recovery systems can use either gravity or forced methods. Gravity systems are generally applicable in shallow groundwater regimes (less than 8 meters or 25 feet) and forced systems are applicable in deep groundwater regimes. The hydraulic conductivity of the waste deposit and surrounding soil media and the time required to accomplish remediation must also be considered in selecting recovery systems. Figure 1-17 gives guidance on which methods are suitable for recovery systems depending on the grain size of the soil. This figure indicates that gravity recovery systems, as well as well points and deep wells, are limited to media with an effective grain size (d_{10}) between 0.1 to 1 mm (0.004 to 0.04 inches) which generally have a hydraulic conductivity between $5x10^{-1}$ to 10^{-3} cm/sec (1420 to 2.8 ft/day) (Table 1-1). For media with effective grain size (d_{10}) between 0.1 to 0.01 mm (0.004 to 0.0004 inches) which generally have a hydraulic conductivity between 10^{-3} to 10^{-5} cm/sec (2.8 to 0.03 ft/day) (Table 1-1), recovery of water may be possible using well points equipped with vacuum pumps. Media with hydraulic conductivity less than 10^{-5} cm/sec (0.03 ft/day) i.e., d_{10} less than 0.01

FIGURE 1-16
DEEP WELL
RECOVERY SYSTEM

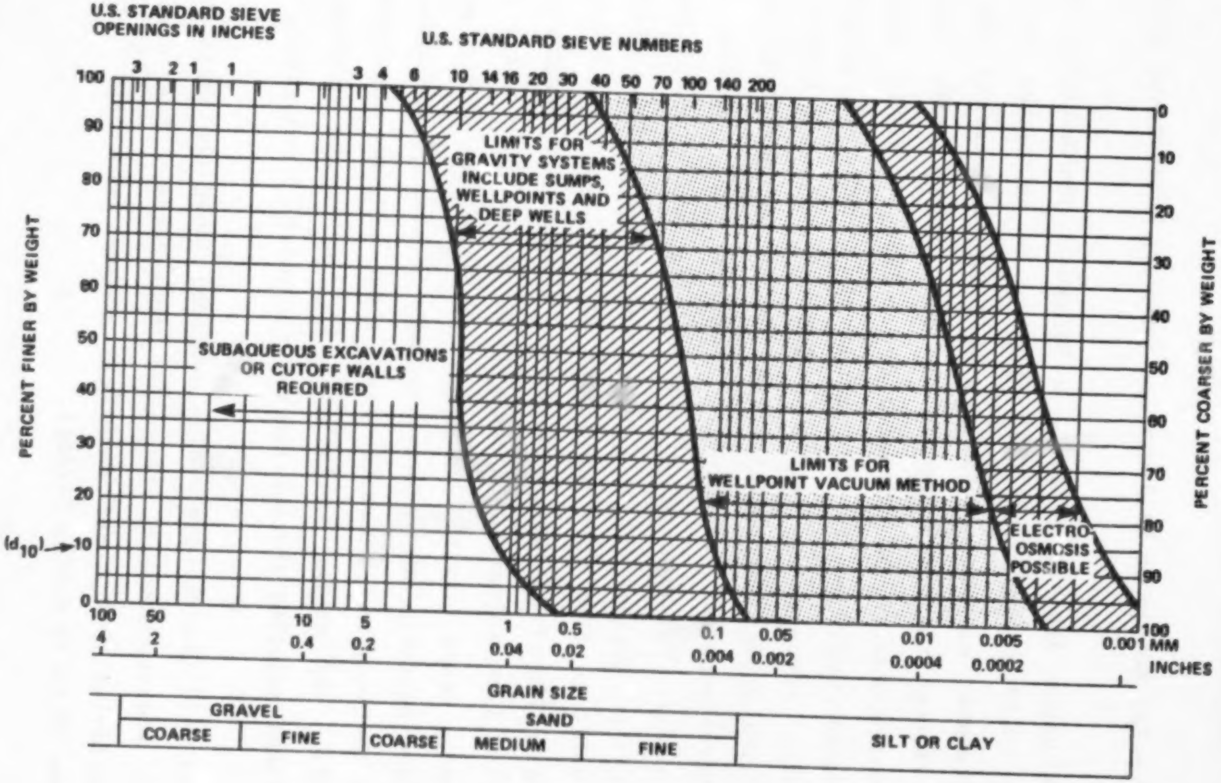

DEEP WELL
WASTE DEPOSIT

PLAN VIEW


DELIVERY SYSTEM
TO TREATMENT
INITIAL GROUNDWATER TABLE
CONE OF DEPRESSION
SCREEN
WASTE DEPOSIT
TURBINE PUMP
DIRECTION OF INDUCED FLOW
CLAY OR BEDROCK

CROSS SECTION

FIGURE 1-17
LIMITS OF RECOVERY METHODS APPLICABLE TO DIFFERENT SOILS



SOURCE: US DEPARTMENT OF THE NAVY, 1982

mm (0.0004 inches) can only be dewatered by means of other enhancement techniques (e.g., electro-osmosis, which is discussed in the following section) used in conjunction with wells or well points.

1.4 Special Method of Delivery and Recovery Enhancement (Electro-Osmosis)

When a waste deposit exhibits a hydraulic conductivity of less than 10^{-5} cm/sec (0.03 ft/day) and the fluid to be extracted is high in inorganic constituents, electro-osmosis may be used to increase the flow rate of the fluid through the waste deposit and surrounding media. Groundwater migration by electro-osmosis is initiated by applying a direct electric potential to electrodes installed in the ground at a selected spacing within the low hydraulic conductivity media. The electric potential applied to the electrodes causes the positive ions in the pore water to move from the anodes (positively-charged electrodes) towards the cathodes (negatively-charged electrodes). The movement of the positive ions develops tension in the media, causes the chemical composition of the groundwater to change, and forces the pore water to flow from the anodes to the cathodes. These actions result in the reduction of the water content of the deposit (Loughney, 1975) or movement of water from injection to recovery wells if these wells form the anodes and cathodes, respectively. Some waste deposits that do not permit application of standard delivery and recovery methods because of low hydraulic conductivities might be rendered treatable when these methods are combined with electro-osmosis. By making wellpoints, the anode and cathode, movement of the treatment solution through the deposit may be accelerated.

Figure 1-17 (in the preceeding section) shows the grain size distribution for which electro-osmosis should be considered. The corresponding hydraulic conductivity for these materials ranges from $1x10^{-5}$ to less than $1x10^{-7}$ cm/sec (0.03 to 0.0003 ft/day).

A site investigation should be performed prior to selecting any injection or recovery system. Once the site conditions are known and it has been determined that the hydraulic conductivity may be enhanced by electro-osmosis, conductivity tests should be performed to determine the electro-osmotic transmission coefficient, k_e (volume of water transmitted through a unit cross section in unit time by application of a potential of 1 volt/cm normal to the cross section). This coefficient is determined in the laboratory or field and used in a Darcy-type equation.

The discharge of a cathode wellpoint, Q_e, may be estimated from the equation (Fruco and Associates, 1966).

$$Q_e = k_e\, i_e\, a_1\, z \tag{1-15}$$

where:

k_e = coefficient of electro-osmotic permeability (length^2/volts x time)
i_e = electrical gradient between electrodes (volts/length)
z = length of electrodes (length)
a_1 = effective spacing of wellpoints (length)

The current required can be estimated from the following empirical equation developed by Maclean and Rolfa (as presented in Loughney, 1975):

$$I_1 = (Ac + B)/t \tag{1-16}$$

where:

I_1 = current required per gram (pound) of water expelled (amps)
t = time
c = clay content of soil, i.e., weight of soil finer than 0.002 mm (0.00008 inches)(percent)
A = constant
B = constant

Current requirements commonly range between 15 and 30 amps per recovery well, and power requirements are generally high. However, regardless of the expense of installation and operation of an electro-osmotic dewatering system, it may be the only effective means of dewatering or permeating certain fine-grained soils.

In an electro-osmotic dewatering system, the depth of the electrodes should be at least 1.5 meters (5 ft) below the bottom of the contaminated deposit that is to be dewatered. The spacing and arrangement of the electrodes may vary, depending on the configuration of the area to be dewatered and the voltage available at the site. Cathode spacings of 8 to 12 meters (25 to 40 ft) have been used, with the anodes installed midway between the cathodes. Electrical gradients of 5 to 13 volts per meter (1.5 to 4 volts per ft) distance between electrodes have been successful in electro-osmotic dewatering. The electrical gradient should be less than about 50 volts per meter (15 volts per ft) of distance between electrodes for long-term installations to prevent loss in efficiency caused by heating of the ground. Applied voltages of 30 to 100 volts are usually satisfactory; a low voltage is usually sufficient if the groundwater has a high mineral content (i.e., high conductivity) (Fruco and Associates, 1966).

Electro-osmosis would only be cost-effective in waste sites having low hydraulic conductivities. Hydraulic conductivities of less than 10^{-7} cm/sec (0.0003 ft/day) prior to initiating electro-osmosis can be made to exhibit hydraulic conductivities in the range of 10^{-5} to 10^{-6} cm/sec (0.03 to 0.003 ft/day) for a gradient of 3 volts per meter (one volt per ft) using this method (Fruco and Associates, 1966). It should be noted that these enhanced hydraulic conductivities are nevertheless very low, i.e., groundwater or leachate flow velocity will still be very slow.

Power consumption is a major limitation on the economic feasibility of the procedure. Use of long term, low power options should be considered when it is possible to do so within the time frame established for the site remediation.

1.5 Comparative Analysis of Alternatives

The application of chemical solutions into a waste deposit to provide in situ treatment or mobilization of contaminants from the deposit requires an appropriate delivery and recovery method. The selection of delivery and recovery techniques requires an understanding of the parameters governing these systems, including site conditions, nature and configuration of the waste deposit, geohydrologic features, and surface hydrologic characteristics.

As discussed in the previous sections, two major delivery and recovery techniques, gravity and forced, are possible. Alternatives that can be considered for delivery and recovery systems are given in Table 1-3. A comparative analysis of gravity and forced systems focusing on parameters affecting selection of these systems and an engineering judgement on the application of each alternative system is presented in this section.

1.5.1 Importance of Various Parameters in Gravity vs Forced Systems

Gravity methods utilize natural gravity forces to effect the delivery and recovery of solutions, while forced methods utilize mechanical mechanisms to deliver or withdraw the solution from the waste deposit. Soil infiltration rates and hydraulic conductivities are key parameters controlling the effectiveness of a gravity method. Pressure head and hydraulic conductivities are the key design criteria for pumped and vacuum type forced methods.

Table 1-4 provides a list of applicable parameters affecting the design of gravity and forced delivery and recovery systems.

1.5.2 Application of Various Systems

The selection of delivery or recovery methods depends primarily on the geohydrologic characteristics of the disposal site. Two matrices (one for delivery systems and one for recovery systems) have been developed in order to guide in the identification of feasible delivery and recovery methods for a

TABLE 1-3

DELIVERY AND RECOVERY SYSTEMS

Delivery/Recovery Techniques	Alternatives
Delivery Systems	
Gravity Methods	Flooding, Ponding, Ditch, Surface Spraying, Infiltration Gallery, Infiltration Bed
Forced Methods	Injection Pipe (open end or slotted)
Recovery Systems	
Gravity Methods	Ditch, Buried Drain
Forced Methods	Wellpoint with Vacuum Wellpoint without Vacuum Deep Well
Electro-Osmosis	

TABLE 1-4

RELATIVE IMPORTANCE OF GEOTECHNICAL PARAMETERS IN GRAVITY AND FORCED SYSTEMS

	Gravity Methods	Forced Methods
1. Hydraulic Conductivity (K)	I	I
2. Infiltration Rate (I_s)	I	NI
3. Application Rate (q_1)	I	LI
4. Configuration of Water Table and Waste Deposit Location (H_c, H_d)	I	LI[1]
5. Time to Reach Saturated Condition (t)	I	LI
6. Homogeneity	I	LI
7. Relation of Hydraulic Conductivity between Waste Deposit and Surrounding Medium	I	LI
8. Relationship between Infiltration Rate and Hydraulic Conductivity	I	NI

NOTE: I = Important
LI = Less Important
NI = Not Important

1 = wellpoints are limited by depth to the watertable

given set of site conditions. These matrices, presented in Tables 1-5 and 1-6 are based on engineering judgement and experience. The major criteria used to identify potentially suitable delivery and recovery systems are discussed in the following subsections.

1.5.2.1 Hydraulic Conductivity

Gravity delivery methods would be applicable for situations in which the waste deposit and surrounding soil media have hydraulic conductivities between 1×10^{-1} cm/sec and 1×10^{-3} cm/sec (280 to 2.8 ft/day). Forced delivery methods would be applicable for situations where hydraulic conductivities are between 1×10^{-3} cm/sec and 1×10^{-4} cm/sec (2.8 to 0.28 ft/day). At a site where the hydraulic conductivity is less than 1×10^{-4} cm/sec (0.28 ft/day), enhancement techniques such as electro-osmosis or hydrofracturing would be required.

In terms of recovery systems, a site where the hydraulic conductivity is between 1×10^{-1} cm/sec and 1×10^{-3} cm/sec (280 to 2.8 ft/day) would be amenable to open ditches and buried drains. Also at such a site, wellpoint and deep well systems would be suitable. The vacuum well point recovery system would be a feasible technique for a site having a hydraulic conductivity between 1×10^{-3} cm/sec and 1×10^{-5} cm/sec (2.8 to 0.03 ft/day). For a waste deposit having a relatively low hydraulic conductivity (below 1×10^{-5} cm/sec or 0.03 ft/day), electro-osmosis may be the only effective recovery method.

1.5.2.2 Depth of Waste Deposit Cover

In general, gravity delivery and recovery methods would be more effective for a shallow waste deposit with a thin cover, while the depth of the waste deposit and cover thickness depth would not affect the application of forced methods (except recovery by wellpoints since these are limited to 5 meters per stage). In practice, gravity delivery and recovery systems are preferred for a waste deposit site having a total depth of waste and cover of less than 5 meters (16 ft). Forced delivery and recovery systems are more suitable for depths greater than 5 meters (16 ft).

TABLE 1-5

MATRIX FOR DELIVERY METHODS

Delivery Methods	Location of the deposit in relation to existing groundwater table			Contamination starts at		Thickness of overlying impermeable layer			Topography (Slope)			Infiltration Rate cm/hr (inches/hr)			Hydraulic Conductivity cm/sec (ft/day)			Depth to Bottom of the Waste Deposit Meters (ft)		
	Unsaturated	Partially Saturated	Saturated	Surface	Subsurface	0	< 1.5m (>5ft)	> 1.5m (>5 ft)	Flat	0-3%	>3%	.1-.2 (.3-5)	.06-.1 (.15-.3)	<.06 <0.15	$10^{-1}-10^{-3}$ (280-2.8)	$10^{-3}-10^{-4}$ (2.8-0.28)	$10^{-4}-10^{-7}$ (0.28-0.0003)	<5 (<16)	5-12 (16-40)	> 12 (>40)
GRAVITY																				
1. Flooding	X	LE	NA	X	X	X	NA	NA	X	X	NA	X	X	NA	LE	NA	NA	X	LE	NA
2. Ponding	X	LE	NA	X	X	X	X	NA	X	X	NA	X	X	LE	X	LE	NA	X	LE	NA
3. Surface Spraying	X	NA	NA	X	X	X	NA	NA	X	X	LE	X	X	NA	LE	NA	NA	X	LE	NA
4. Ditches	X	LE	NA	NA	X	X	X	NA	X	X	X	X	X	X	X	LE	NA	X	LE	NA
5. Infiltration Galleries	X	LE	NA	NA	X	X	X	X	X	X	X	X	X	X	X	LE	NA	X	X	NA
6. Infiltration Bed	X	LE	NA	NA	X	X	X	X	X	X	NA	X	X	X	X	LE	NA	X	X	NA
FORCED																				
1. Injection Pipes	X	X	X	$X^{(1)}$	X	X	X	X	X	X	X	X	X	X	X	X	$X^{(2)}$	X	X	X

X = Applicable
LE = Less Effective
NA = Not Applicable
(1) = May need combined gravity and forced delivery.
(2) = Applicable with electro-osmosis.

TABLE 1-6

MATRIX FOR RECOVERY METHODS

Recovery Methods	Depth To Groundwater			Hydraulic Conductivity		
	0-5 m (0-16 ft)	5-12m (16-40 ft)	>12 m (>40 ft)	$>10^{-1}-10^{-3}$ cm/sec (>280-2.8 ft/day)	$10^{-3}-10^{-4}$ cm/sec (2.8-0.28 ft/day)	$10^{-4}-10^{-7}$ cm/sec (0.28-0.003 ft/day)
GRAVITY:						
Open Ditches and Trenches	X	NA	NA	X	LE	NA
Porous Drains	X	NA	NA	X	LE	NA
FORCED:						
Wellpoint	X	X	NA	X	LE	NA
Deep Well	NA	X	X	X	LE	NA
Vacuum Well Point	X	X	NA	NA	X	LE
Electro-osmosis	X	X	X	NA	NA	X

X = Applicable
LE = Less Effective
NA = Not Applicable

Design criteria related to the configuration of the waste deposit and its surrounding media can be summarized as follows:

1. Gravity delivery methods are most effective if the waste deposit is situated in the unsaturated zone, and at the surface or at a relatively shallow depth (less than 5 meters or 16 feet).

2. If the deposit is covered with a thin layer of impervious material (less than 1.5 meters or 5 feet) gravity delivery might require excavation but would probably still be more cost-effective than forced delivery.

3. Open ditches are generally limited to depths not exceeding 4-5 meters (13 to 16 feet) below ground level. The trench depth of buried drains for groundwater recovery from a waste disposal site should also be limited to a maximum of 16 feet below ground level.

4. A stage of well points would be capable of draining a deposit of about 5 meters (16 feet) in depth. Draining a deposit of greater than 5 meters (16 feet) generally requires a multi-stage installation of wellpoints and vacuum pumps to assure the maintenance of the maximum vacuum in the column. In this case, down-hole pumps may be more cost-effective.

5. For deep groundwater conditions, more than 8 meters (25 feet), it may be more practical to use deep recovery wells with turbine or submersible pumps.

6. Deep well systems are particularly suited for dewatering large areas at greater depth where large volumes of fluid must be removed.

1.5.2.3 Climate

The influence of climate is more significant for gravity delivery and recovery systems than for the forced methods. Freezing and frost penetration may preclude the operation of gravity delivery and recovery systems, particularly flooding, ponding, ditches and surface spraying methods. Subsurface spreading methods may be suitable where ground freezing is a recurring problem. Infiltration galleries or beds can be installed under the freezing zone, thereby permitting year-round application of solution. A forced delivery system, unlike the gravity systems, is conceptually independent of surface topography and climate and can be designed to accommodate any waste deposit configuration.

1.5.2.4 Relationship Between Waste Deposit and Soil Medium

The most important relationship between the waste deposit and the surrounding soil medium is that of their hydraulic conductivity values. If the waste deposit has a lower hydraulic conductivity than the surrounding soil, gravity delivery would not be reliable, because the solution would most probably bypass the waste deposit. Therefore forced injection of reactant solution directly into the waste deposit would be required. Gravity delivery methods are thus most effective in relatively homogeneous deposits where the applied solution can be evenly distributed throughout the deposit. In a heterogeneous environment, the waste deposit may not be effectively reached by gravity delivery methods.

The hydraulic gradient formed by the natural conditions cannot be easily altered in gravity delivery methods. With forced delivery methods, the hydraulic gradient can be increased by increasing the injection pressure. This pressure would increase the transmission rate of the applied solution through the medium.

Using gravity delivery methods, the applied solution will generally have to travel from the point of application through the overlying soil to reach a subsurface waste deposit. Forced delivery methods allow direct application of reactant solution into a waste deposit, eliminating attenuation or reaction of the solution with the overlying soil.

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SECTION 2

BIODEGRADATION

2.1 Introduction

Recent developments in applied microbiology (Bitton and Gerba, 1984; API, 1982; Doggett, 1983; Jhaveri and Mazzacca, 1983; Kellogg et al, 1981; Kopecy, 1983; Krupka and Thibault, 1980; Litchfield and Clark, 1973; Zitrides, 1978) have made in situ biological treatment of hazardous organic materials in soil, water, and groundwater a potentially cost effective alternative to chemical or physical methods of site reclamation. Biological treatment involves the use of native microbes, selectively adapted bacteria or genetically altered microorganisms that have been modified through specific gene mutation or genetically assisted molecular breeding to degrade a variety of organic compounds. Biodegradable compounds include industrial surfactants, organic solvents, crude and refined petroleum products, pesticides and herbicides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons and other classes of organic compounds (Bitton and Gerba, 1984; Kobayashi and Rittman, 1982) as discussed below. The biological treatment process usually involves the addition of nutrients and oxygen, and may take place completely within the deposit or (more commonly) partly above ground in environmentally-controlled bioreactors and partly within the waste deposit. Typically, contaminated groundwater is recirculated from downgradient recovery wells, through bioreactors and conditioning processes (e.g. aerators) at the surface, and reinjected at upgradient locations for further in situ degradation.

This section discusses a number of organic waste treatment methods that involve the use of microbial agents. Processes of waste biodegradation are identified that may be used as the sole treatment or in conjunction with chemical or physical methodologies or both. These methods are representative of an emerging technology and significant advances can be expected in the near term. It should be recognized that as these existing methods are superseded by more advanced techniques, new procedures should be considered in future strategies concerning the in situ treatment of wastes. The information included on biological methods of waste stabilization was obtained from published reviews, literature, reports on demonstration studies and personal communications with commercial firms that are actively developing this technology. Methodology guidelines have been developed from these sources.

2.2 Analysis of Data

2.2.1 Microbial Mechanisms of Catabolism

It has long been recognized (Atlas, 1981; Horvath, 1972; Zobell, 1946) that many microorganisms have the ability to utilize hydrocarbons as the sole source of carbon and energy. These microbial communities react to the a wide range of naturally occurring and anthropogenic (synthetic) hydrocarbons.

Hydrocarbons are catabolized (broken down to simpler substances) by microorganisms using three general mechanisms (Atlas, 1981; Focht and Chang, 1975; Sokatch, 1969; Stanier et al, 1976). These are aerobic respiration, anaerobic respiration, and fermentation. In general, aerobic degradation processes are more often used for biodegradation because the degradation process is more rapid and more complete, and problematic end products (methane, hydrogen sulfide) are not produced. However, anerobic degradation is important for dehalogenation (Bouwer and McCarty, 1983).

In aerobic respiration, organic molecules are oxidized to carbon dioxide (CO_2) and water or other end products using molecular oxygen as the terminal electron acceptor. Oxygen may also be incorporated into intermediate products of microbial catabolism through the action of oxidase enzymes, making them more susceptible to further biodegradation. Microorganisms catabolize hydrocarbons by anaerobic respiration in the absence of molecular oxygen using inorganic substrates as terminal electron acceptors. In anaerobic respiration, CO_2 is reduced to methane (CH_4), sulfate (SO_4^{-2}) to sulfide (S^{-2}), and nitrate (NO_3^-) to molecular nitrogen (N_2) or ammonium ion (NH_4^+). Hydrocarbon sources are degraded by fermentation using substrate level phosphorylation as the terminal electron acceptor. Fermentation results in a wide variety of end products including carbon dioxide, acetate, ethanol, proprionate, butyrate, etc.

In most cases, naturally occurring microbial activity can decompose organic materials of both natural and synthetic origin to harmless or stable forms or both by aerobically mineralizing them to CO_2 and water, or anaerobically decomposing them to CO_2, CH_4 and water (Alexander, 1981; Atlas, 1981; Bitton and Gerba, 1984; Boethling and Alexander, 1979a and 1979b; Evans, 1977; Kobayashi and Rittman, 1982; Perry, 1979; Sokatch, 1969; Stanier et al, 1976; Zobell, 1946). Some anthropogenic compounds can appear relatively refractory to biodegradation by naturally occurring microbial populations because of the interactions of environmental influences, lack of solubility, absence of required enzymes or other factors as discussed by Alexander (1981). However, the use of properly selected or engineered microbial populations, maintained under environmental conditions most conducive to their metabolic activity (including microbial growth and continued catabolic breakdown of waste compounds), can be an important means of biologically transforming or degrading these otherwise refractory wastes (Doggett, 1983; Evans, 1977; Horvath, 1972; Kaplan et al., 1982; Knap and Williams, 1982; Kobayashi and Rittman, 1982; Krupka and Thibault, 1980; Nasset, 1983; Stoddard et al, 1981; Thibault and Elliott, 1983; Zitrides, 1978). Indeed, it has been postulated by Horvath (1972) that the concept of molecular recalcitrance (Alexander, 1981) to degradation by microorganisms may not be valid.

2.2.2 Development of Microbial Agents

Microbial systems are available to treat a wide variety of hydrocarbons (Bitton and Gerba, 1984; Atlas, 1981; Kobayashi and Rittman, 1982; Kopecky, 1983; Zitrides, 1978) including chlorinated and unchlorinated alkanes, aromatics and polycyclic aromatics, nitrosamines, pesticides and herbicides, phthalate esters, etc. Biological agents available to degrade these compounds may occur as, or arise from, naturally occuring microorganisms (Kobayashi and Rittman, 1982). In addition, biological agents may be acclimated to specific organic materials or mixtures through a system adaption or mutation/adaptive regimen (Bitton and Gerba, 1984; Kobayashi and Rittman, 1982; Kopecky, 1983; Zitrides, 1978), or through the use of plasmid insertion. Microbial strain or system acclimation may include enzyme induction, strain selection and mutation. The use of specific nutrients (vitamins, nitrogen, phosphorus, trace elements, etc.) to encourage microbial growth, and surfactants to increase substrate solubility can also produce novel biological agents or systems for the degradation of organic pollutants (Kobayashi and Rittman, 1982; Kopecky, 1983; Zitrides, 1978).

Systems have been developed to treat subsurface soils, groundwaters, surface spills, lagoons, ponds and other surface waters. These systems include the use of activated sludge treatment (Kobayashi and Rittman, 1982), fixed film reactors (Kobayashi and Rittman, 1982), subsurface injection (Kobayashi and Rittman, 1982; Zitrides, 1978), groundwater pumping for surface treatment (Zitrides, 1978), and surface application combined with soil turning (Kopecky, 1983; Zitrides, 1978). Several commercial firms have developed proprietary strains of microorganisms or are capable of adapting native populations for use in waste site renovation, and have also developed the engineering technology and treatment systems required for these methods. The kinetics of biodegradation, as well as design considerations for the implementation of biodegradation systems (i.e., hydraulic design, aeration/oxygenation systems, use of hydrogen peroxide, ozone and other oxygen sources, nutrient addition, and operation and maintenance requirements) are described in Repa and Kufs (1985), A D Little (1983), Jhaveri and Mazzacca (1983), and USEPA (1984d).

Appendix A identifies specific native microflora, microbial consortia, laboratory derived strains and commercially available microorganisms and the organic compounds that they are able to transform or degrade. The environmental conditions that prevail during the course of treatment are described when data are available. Appendix A also identifies catabolic end products, degradation rates and treatable concentrations as reported in the literature. Appendix A indicates that almost every class of organic compound can be degraded by some microorganism. These microbes include representatives from the obligate anaerobes, anaerobic bacteria, heterotrophic bacteria, oligotrophic bacteria, phototrophic bacteria, actinomycetes and fungi.

Bacteria isolated from the environment are often identified to the genus level only, or if speciated are assigned a strain number. This is done to avoid confusing them with other members of the genus or species that have not demonstrated the abilities associated with the organism identified by the strain number. In other instances, an organism may be identified by the plasmid it carries. Plasmids are extrachromosomal, inheritable pieces of DNA (also called episomes) which can be transmitted to other cells. These episomes are identified by initials which may indicate the substrates they degrade (such as TOL plasmid specifying toluene and xylene degradation or SAL plasmid specifying salicylate degradation) or simply by laboratory code numbers (such as pAC25 specifying 3-chlorobenzoate degradation). Bacteria characterized by strain or plasmid code identifier in the literature as having the capacity to degrade specific compounds or classes of compounds are identified in this document by that strain or plasmid code.

Obligate anaerobic bacteria are represented by hydrolytic bacteria (which catabolize saccharides, proteins, lipids); hydrogen producing acetogenic bacteria (which further break down the products of hydrolytic bacteria, e.g., fatty acids and neutral end products); homolactic bacteria (which catabolize multicarbon compounds to acetic acid); and methanogenic bacteria (which break down acetic acid to methane and carbon dioxide). The strict anaerobes require anoxic environments and oxidation-reduction potential of less than -0.2 volts. These microorganisms are commonly referred to as methanogenic consortia and are found in anaerobic sediments or sewage sludge digesters. These organisms play an important role in reductive dehalogenation reactions, nitrosamine degradation, reduction of epoxides to olefins, reduction of nitro groups and ring fission of aromatic structures (Evans, 1977; Kobayashi and Rittman, 1982).

The most commonly isolated microbes in areas contaminated with hydrocarbons are heterotrophic bacteria (i.e., bacteria for which complex organics, rather than inorganic materials, are the chief source of nutrients) represented by the genera Pseudomonas, Achromobacter, Arthrobacter, Acinetobacter, Micrococcus, Vibrio, Brevibacterium, Corynebacterium and Flavobacterium. The first five genera are of special importance in hydrocarbon degradation (Kobayashi and Rittman, 1982; Ornston, 1971; Rogers et al, 1981). The genus Pseudomonas, an environmentally ubiquitous bacteria, has proven to be especially versatile in its ability to readily adapt to a wide variety of substrates (Ornston, 1971). Pseudomonads have been adapted and genetically engineered to degrade an expanding array of substrates including, among others, halogenated aromatic ring structures (Evans, 1977; Furukawa and Chakrabarty, 1982; Kellogg et al, 1981; Kilbane et al, 1982; Ornston, 1971; Serdar et al, 1982; Zitrides, 1978). Members of this genus are able to catabolize these compounds aerobically using oxygen as the terminal electron acceptor or anaerobically by nitrate respiration.

Oligotrophic bacteria are defined as microbes that live under conditions of low productivity (carbon flux of less than one mg/l/day). The Caulobacters (Poindexter, 1981) are the best known group of obligate oligotrophics but a number of bacteria, fungi or actinomycetes are capable of adapting to an existence under these conditions (Kobayashi and Rittman, 1982). These organisms are found in biofilms and appear to have multiple inducible enzyme systems and are therefore capable of metabolizing a wide variety of substrates.

Phototrophic microorganisms (i.e., those which obtain energy from sunlight) include algae, cyanobacteria (blue-green algae) and photosynthetic bacteria. These organisms are involved in biological transformations rather than degradation. They are important in that the metabolic products they form from otherwise refractory organic compounds become the growth substrate of heterotrophic bacteria (Kobayashi and Rittman, 1982).

Actinomycetes are morphologically similar to both bacteria and fungi and are known to attack a wide variety of complex organic compounds including phenols, pyridines, glycerides, sterols, halogenated and unhalogenated aromatic compounds, paraffins, other long chain organics and lignocellulose. They are obligate aerobes and are capable of growth under oligotrophic conditions. They can grow under wide extremes of pH and temperature and are resistant to desiccation (Kobayashi and Rittman, 1982). Fungi have non-specific enzyme systems that enable them to degrade or transform hydrocarbons of complex structure or chain length. These organisms play an important role in the degradation of aromatic structures including polychlorinated biphenyls (Bumpus et al., 1985). However, the metabolism of these compounds is often incomplete and requires an association with bacterial populations to assure complete mineralization (Kobayashi and Rittman, 1982).

2.2.3 Factors Affecting The Use Of Microbial Agents

Generally, microorganisms require adequate levels of inorganic and organic nutrients, growth factors (vitamins, magnesium, copper, manganese, sulfur, potassium, etc.), water, oxygen, carbon dioxide and sufficient biological space for survival and growth. One or more of these factors is usually in limited supply and the various microbial competitors adversely affect each other through the struggle for these limiting factors (Rosenzweig and Stotzkey, 1980). Additional factors which can influence microbial biodegradation rates include microbial inhibition by the test compound, the number and physiological state of the organisms as a function of available nutrients, the seasonal state of microbial development, predators, pH (optimum range is 6-8), and temperature (Fannin et al., 1981). The optimal temperature for aerobic biodegradation processes is 68°F to 97°F (20-37°C). However, groundwater temperatures are below this range in many parts of the United States, leading to suboptimal biodegradation rates (Repa and Kufs, 1985 provides a map of typical groundwater temperatures in the United States). Interactions between these and other potential factors can cause wide variations in degradation kinetics.

The studies of Liang et al. (1982) have indicated that there may be risk associated with the use of biological agents in organic waste treatment. Components of this risk include the probabiliites of release, survival and growth of non-indigenous microbes, and the consequent occurrence of some undesirable environmental or ecological change. An analysis of risk should be performed for these microorganisms, and any other biological agent intentionally used for waste treatment, to insure that adverse environmental impacts will not result from their use.

2.2.4 Susceptibility of Various Chemical Classes to Biodegradation

This discussion evaluates the various biological treatment technologies inducible from naturally occurring microbial ecosystems or available commercially, that are applicable to the degradation of organic waste materials, including halogenated and unhalogenated alkanes, aromatics and polycyclic aromatics, pesticides and herbicides, nitrosamines, phthalate esters, and many others. The catabolic reactions leading to the biodegradation of organic materials are fairly well known and can be found in several reviews (Atlas, 1981; Bitton and Gerba, 1984; Evans, 1977; Kobayashi and Rittman, 1982; Ornston, 1971). Studies by Kobayashi and Rittman (1982) and others have demonstrated that properly selected microbial populations and the maintenance of environmental conditions most favorable to their metabolic activity can degrade significant quantities of organic materials. The role of microorganisms in hydrocarbon biodegradation is so extensive that Kobayashi and Rittman (1982) concluded that attempts to generalize the relationship between chemical structure, substitutions, chain length or molecular size and biodegradability have so many exceptions that they should be considered only as broad guidelines.

The relative biodegradability of specific organic compounds can be estimated based on the ratios of various parameters describing their oxygen requirement for decomposition. Specifically, the ratios of the 5-day biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD), or the 21-day BOD (BOD_{21}) to ultimate oxygen demand (UOD), indicate what proportion of compounds can be degraded biologically (estimated by BOD) compared to the biorefractory portion which would require chemical decomposition (estimated by COD or UOD). BOD_5/COD ratios and BOD_{21}/UOD ratios (also called refractory index, or RI) for various compounds are listed in Repa and Kufs (1985). In general, phenols, alcohols, esters, aldehydes, carboxylic acids and some simple aromatic compounds (benzene, toluene, napthalene) appear to have relatively high degradability using these relationships, while halogenated phenols, aliphatics and aromatics appear to be less readily biodegraded (Repa and Kufs, 1985).

2.2.4.1 Non-Halogenated Branched and Straight Chain Alkanes

Atlas (1981) discussed the microbial degradation of n-alkanes with chain lengths up to C_{44}. The initial degradation produces a primary alcohol, followed by an aldehyde and a monocarboxylic (fatty) acid. The carboxylic acid is further oxidized to a shorter-chain fatty acid. The catabolism of long chain carboxylic acids can be inhibited by shorter chain carboxylic acids, thus preventing further degradation of the longer chain carboxylic acids (Atlas and Bartha, 1973).

Straight chain and branched alkanes are readily degraded by a wide variety of soil and salt water bacteria, and activated sludge microorganisms (Hill and McCarty, 1967; Kobayashi and Rittman, 1982; Kobayashi and Tchan, 1978; Murray and Van der Berg, 1981; Ornston, 1971; Wolfe et al.,1980; Yordy and Alexander, 1980). Organisms identified in the literature include pseudomonads (de Smet et al., 1981; Litchfield and Clark, 1973; Ornston, 1971; Perry, 1979), actinomycetes (Perry, 1979), yeast microorganisms (Perry, 1979), Bacillus (de Smet et al., 1981), Corynebacterium (de Smet et al., 1981), methylotrophic bacteria (Mancinelli et al., 1981), and activated sludge organisms (Kobayashi and Rittman, 1982). These alkanes, especially those with shorter chains, often occur in nature as plant and animal byproducts. Microorganisms more readily adapt to the catabolic use of these compounds than to more complex structures, esentially because of their simple form and availability in the environment. Native populations of microorganisms have been shown to degrade aliphatic hydrocarbons ranging in concentration from 1 ppm or less up to approximately 1,000 ppm or more. Within the concentration range specified, the biodegradation of these aliphatics appears to be dependent on the solubility of the hydrocarbon in the environment (Atlas, 1981). The ability of these organisms to degrade higher concentrations of specific aliphatics can be enhanced by the process of adaptation or genetic manipulation (Doggett, 1983; Kobayashi and Rittman, 1982; Kopecky, 1983; Ornston, 1971; Zitrides, 1978).

Litchfield and Clark (1973) found that significant populations of bacteria are present in groundwater contaminated with hydrocarbons including gasoline, fuel oil, and other petroleum products. They found that waters containing less than 10 ppm hydrocarbons generally had populations of less than 10^3 organisms per ml while waters with hydrocarbon concentrations in excess of 10 ppm generally supported populations on the order of 10^6 organims per ml. Species were identified as belonging mostly to the genera Pseudomonas and Arthrobacter.

Highly branched isoprenoid alkanes are degraded to dicarboxylic acids. Methyl branching, which generally increases the resistance of hydrocarbons to microbial attack, requires that microorganisms use additional degradational mechanisms (Atlas, 1981). Representative acyclic hydrocarbons subject to biodegradation are shown in Appendix A.

Mutants of Pseudomonas, Aerobacter and Micrococcus have been shown, under laboratory conditions, to be capable of the total degradation of nitriles, cyanides and amines at concentrations ranging from 250 ppm to 500 ppm in a matter of hours. When used in a bioreactor renovation of waste water, these organisms were capable of degrading acrylonitrile at concentrations ranging from 100 to 1,000 ppm to less than 1 ppm over a period of 3 months (Krupka and Thibault, 1980; Nassef, 1983; Zitrides, 1978). The degradation of specific compounds within these groups, concentrations listed, degradation times and microorganisms involved are identified in Appendix A.

2.2.4.2 Aromatic Compounds and Phenols

Extensive studies on the catabolism of aromatic compounds by microorganisms have identified many of the pathways and mechanisms involved in their degradation. These cyclic compounds have been reported to be substrates for cooxidation with the formation of an alcohol or ketone (Atlas, 1981; Horvath, 1972; Jacobson et al., 1980; Perry, 1979). Substituted cyclic compounds are more easily degraded than unsubstituted forms, particularly if the substituent is an n-alkane of adequate chain length (Atlas, 1981; Perry, 1979). Microbial attack in such cases usually occurs first on the substituent, producing an intermediate product such as cyclohexane, carboxylic acid or similar compound.

Bacterial (procaryotic) degradation of aromatic compounds usually involves the formation of a diol, followed by ring cleavage and the production of a diacid (Atlas, 1981; Evans, 1977; Ornston, 1971). Eucaryotic organisms, in contrast, oxidize aromatic compounds to the trans diol (Atlas, 1981). Aromatic compounds can be degraded both aerobically and anaerobically (Atlas, 1981; Evans, 1977; Ornston, 1971). Microbial systems capable of degrading various aromatic compounds are identified in Appendix A by compound.

Degradation rates for cyclic aliphatics and aromatic hydrocarbons by native microbes are slower than for acyclic compounds. Native microorganisms will completely or partially degrade these compounds at concentrations below 100 mg/l over a period of 10 to 90 days (Horvath, 1972; Rogers et al., 1981; Rubin et al., 1982). Little data are available concerning mutant bacterial degradation rates on unsubstituted aromatic hydrocarbons. However, genetically altered strains of Psuedomonas, Alcaligenes or Micrococcus have been shown in the laboratory to completely degrade substituted aromatics at concentrations of 200 to 500 ppm over an interval of several hours to a few days (King and Perry, 1975; Krupka and Thibault, 1980; Marinucci and Bartha, 1979; Nassef, 1983; Pfaender and Bartholomew, 1982; Zitrides, 1978). Specific cyclic and aromatic hydrocarbons which have been shown to be susceptible to microbial attack are identified by compound in Appendix A. Also identified are the microbial communities or specific microbes that are capable of degrading these compounds.

2.2.4.3 Polycyclic Aromatic Hydrocarbons

Microbial degradation of polycyclic aromatic hydrocarbons (PAH) compounds have been identified (Atlas, 1981; Cohen and Gabriele, 1982; Herbes, 1981; Kobayashi and Rittman, 1982; Sherrill and Sayler, 1980). However, uniform degradative pathways, comparable to those for the aliphatic and aromatic compounds, have not yet been determined (Atlas, 1981). Among the naturally occurring systems which degrade these compounds are: the fungi Polyporus versicola and Poria monticola which have the capacity to degrade lignite coal (Cohen and Gabriele, 1982); the microbial transformation of anthracene and benz(a)anthracene by stream water and sediment bacteria (Herbes, 1981); and the biodegradation of phenanthrene in fresh water environments (Sherrill and Sayler, 1980). These organisms are usually found downstream of surface water pollution sites (Furukawa and Chakrabarty, 1982; Shiaris et al., 1980). Rates of PAH biodegradation by naturally occurring microbial populations are relatively slow when compared to degradation rates for aliphatic and aromatic compounds. The degradation rates of PAH have been shown to be directly related to historic environmental pollution of the sampling site, the length of biodegradation assessment, temperature and the molecular size of the substrate (Sherrill and Sayler, 1980). Transformation rates in microbial communities shift slowly in response to changes in PAH concentration, but have been shown to remain elevated for more than a year after the removal of the PAH source (Herbes, 1981).

Microbial degradation of two and three ring PAH in the environment has been demonstrated (Aranha and Brown, 1981; Brilon et al., 1981b; Cerniglia et al., 1980; Doggett, 1983; Furukawa and Chakrabarty, 1982; Kiyohara et al., 1982; Knap and Williams, 1982; Kobayashi and Rittman, 1982; Reichartdt et al., 1981). Where identified, PAH concentrations were at or below 100 ppm. Rates of degradation in the environment were highly variable. Native stream bacteria were shown to degrade anthracene (presumably at trace concentrations) over a period of 64 days (Furukawa and Chakrabarty, 1982; Kobayashi and Rittman, 1982). However, a plasmid assisted Alcaligenes was capable of degrading this compound in one to three days (Kiyohara et al., 1982). Native soil bacteria were shown to degrade 100 ppm of naphthalene in 48 hours (Aranha and Brown, 1981). The substituted and unsubstituted forms of napthalene are also degraded by Pseudomonas aerobically (Brilon et al., 1981a) and by phototrophic bacteria anaerobically (Cerniglia et al., 1980). Biphenyl was found to be degraded aerobically by plasmid assisted strains of Acinetobacter and Arthrobacter (Furukawa and Chakrabarty, 1982), by Alcaligenes aerobically in one to three days (Knap and Williams, 1982) and by Beijerinkia (Kobayashi and Rittman, 1982).

2.2.4.4 Halogenated Organic Compounds

Halogenation is often implied as the reason for the presistence of an organic compound in the environment. Some of the characteristics that promote environmental persistence include: the location of the halogen atom on the organic compound; the halide involved; and the extent of halogenation (Kobayashi and Rittman, 1982). Anaerobic reductive dehalogenation (removal of a halogen atom by oxidation-reduction), either biological or abiological, has been identified as the critical factor in the biodegradation or chemical transformation of halogenated organics (Bouwer and McCarty, 1983a; Bouwer and McCarty, 1983b; Edgehill and Finn, 1983; Guenzi and Beard, 1967; Hill and

McCarty, 1967; Kallman and Andrews, 1963; Kobayashi and Rittman, 1982; Marinucci and Bartha, 1979; Reichartdt et al., 1981; Schreiber et al., 1980). Reductive dechlorination is reported to be significant only when the environmental oxidation-reduction potential (E_h) is at or below 0.35V, with the exact requirements dependent upon the compound involved (Kobayashi and Rittman, 1982). Kobayashi and Rittman (1982) report that compounds degraded via anaerobic reductive dechlorination include many pesticides as well as one and two carbon halogenated aliphatic compounds. However, it is important to note that polychlorinated biphenyls and halogenated benzenes have been found to be degraded only under aerobic conditions (Kobayashi and Rittman, 1982).

A great deal of concern has been expressed concerning the persistence of organic pesticides in the environment, particularly the more persistent chlorinated pesticides. Hill and McCarty (1967) report that although these compounds are resistent to aerobic decomposition they degrade more quickly under biologically active anaerobic conditions. This degradation may be a complete mineralization or a partial degradation to other organic end products (Guenzi and Beard, 1967; Hill and McCarty, 1967; Kallman and Andrews, 1963).

One and two carbon halogenated aliphatic organic compounds at trace concentrations were found to be subject to dehalogenation and degradation under anaerobic but not aerobic conditions (Bouwer and McCarty, 1983b; Bouwer et al., 1981; McCarty et al., 1981). Several one and two carbon halogenated aliphatic organic compounds present at low concentrations (less than 100 ug/l) were degraded under methanogenic conditions in a continuous flow fixed film biological reactor. Greater than 90 percent biodegradation was observed after two days under continuous flow methanogenic conditions (Bouwer and McCarty, 1983a).

A number of halogenated aromatic and aliphatic compounds have been reported to be dehalogenated in sewage (DiGeronimo et al, 1979; Jacobson and Alexander, 1981) and soil (Edgehill and Finn, 1983; Marinucci and Bartha, 1979). Jacobsen and Alexander (1981) have reported the dechlorination of 4-chloro-3, 5-dinitro- benzoic acid as a result of microbial growth both in the light (in the absence of added nutrients) and in the dark (in the presence of acetate).

Axenic (pure) bacterial cultures of Chlamydomonas and sewage microfauna release chlorine from the compound and the latter produces alpha hydroxymuconic semialdehyde as an endproduct. This material reportedly serves as a substrate for further metabolism by a strain of Streptomyces (Jacobson and Alexander, 1981). The degradation of 1,2,3- and 1,2,4-trichlorobenzene has been reported in soils with CO_2 evolution (Marinucci and Bartha, 1979).

Pentachlorophenol degrading bacteria of the genus Arthrobacter, capable of the complete mineralization of the compound, have recently been isolated from soil, water and sewage (Stanlake and Finn, 1982). Direct inoculation of Arthrobacter cells into pentachlorophenol contaminated soils reduced the half-life of the pesticide from two weeks to less than one day, using 10^6 Arthrobacter cells per gram of dry soil at 30°C (Edgehill and Finn, 1983).

Microorganisms in sewage have been reported to degrade 3,4-dichlorobenzoates, meta-, para- and orthobenzoates (Di Geronimo et al., 1979), and a 3-chlorobenzoate grown strain of Pseudomonas sp. B13 readily degrades monofluorobenzoates (Schreiber et al., 1980).

Recent advances in microbial genetics have shown that improved degradation of halogenated hydrocarbons can be achieved with constructed strains (Schwien and Schmidt, 1982). In this study a Pseudomonas strain B13 able to degrade 3-chlorobenzoate and 4-chlorophenol, could transfer the ability to degrade chlorocatechols to an Alcaligenes strain A2 recipient capable of growing on benzoate and phenol. The transconjugant was able to use all three isomeric chlorophenols, a property not possessed by either parent.

Chlorinated and polychlorinated biphenyls have been shown to be degraded by a variety of plasmid assisted bacteria (Doggett, 1983; Furukawa and Chakrabarty, 1982; Kobayashi and Rittman, 1982; Reichartdt et al., 1981) with the rate of degradation being inversely proportional to the level of chlorination. Organisms capable of degrading chlorinated biphenyls include Acinetobacter (Furukawa and Chakrabarty, 1982), Arthrobacter (Reichartdt et al., 1981), Pseudomonas, Flavobacter, Archromobacter, Chromobacter and Nocardia (Kobayashi and Rittman, 1982). Compounds in this category which have been shown to be degraded microbiologically are identified along with the agent of degradation in Appendix A.

Degradation of chlorinated biphenyls have been observed in a mixed marine microbial community with estimated turnover rates of one year at concentrations of 0.1 ug/liter or less, and higher turnover times probable at higher concentrations (Reichartdt et al., 1981). However, an Arthrobacter strain M5 contaminant of an Acinetobacter strain P6 culture grown on biphenyl and chlorinated biphenyls showed properties similar to the P6 strain (Furukawa and Chakrabarty, 1982) as a result of a presumed plasmid transfer. The Acinetobacter P6 strain can degrade 33 pure isomers of chlorinated biphenyl including di-, tri- and tetrachlorobiphenyls. A combined culture of the chlorinated biphenyl degrading P6 and M5 strains and genetically constructed mono- or dichlorobenzoate utilizing pseudomonads (harboring the TOL, pAC25, pKF1, pAC21 and pAC30 plasmids which regulate the degradation of these aromatic compounds) allowed greater than 98 percent utilization of mono- and dichloro-biphenyls, with the liberation of equivalent amounts of chloride ions. Once dechlorinated, these compounds are degraded by mechanisms as previously described. Appendix A describes those systems capable of degrading chlorinated hydrocarbons.

2.2.4.5 Herbicides And Pesticides

Some herbicides and pesticides undergo fairly rapid decomposition in anaerobic ecosystems (Guenzi and Beard, 1967; Hill and McCarty, 1967; Kallman and Andrews, 1963; Lewis and Holm, 1981; Reddy and Sethunathan, 1983) and this ability can be enhanced through genetic modifications (Chatterjee et al., 1982; Kellogg et al., 1981; Kilbane et al., 1982; Serdar et al., 1982). Microorganisms can also degrade these materials through cometabolism (i.e., not using these organics as a primary nutrient, but degrading them as an ancillary action of normal metabolic activity) (Fogel et al., 1982; Jacobson et al., 1980; Patil et al., 1972). Chlorodimeform has been shown to be hydrolyzed by Chlorella and Oscillatoria to toluedide, which was deformylated to yield toluedine followed by fission of the aromatic nucleus (Benezet and Knowles, 1981). Microorganisms were able to accomplish the complete or partial degradation of lindane, heptachlor, endrin, aldrin, heptachlor epoxide, DDT, DDD and dieldrin in anaerobic digester sludge (Hill and McCarty, 1967). DDT is converted to DDD by yeast (Guenzi and Beard, 1967; Kallman and Andrews, 1963). Low concentrations of methyl parathion are degraded under aerobic conditions by aufwuchs (attached to a substrate rather than free-floating) bacteria (Lewis and Holm, 1981). Endosulfan can be degraded by 16 fungi, 15 bacteria and 3 actinomycetes (Martens, 1976). Parathion is mineralized by bacteria in the rice rhizosphere under anaerobic (flooded) and aerobic (non-flooded) conditions (Reddy and Sethunathan, 1983), and various organophosphate insecticides have been cleaved under aerobic conditions and mesophillic temperatures (Rosenberg and Alexander, 1979). In addition, the cometabolism of trifuralin, profluralin, fluchloralin and nitrofen (Jacobson et al., 1980) methoxychlor (Fogel et al., 1982), DDT, dieldrin, aldrin and endrin (Patil et al., 1972) in various environments has been reported. The degradation of these compounds by microbes is identified in Appendix A. When identified in the literature, general environmental conditions and byproducts have also been compiled.

Recent studies have shown that Pseudomonas cepacia AC1100 was capable of using 2,4,5,-trichlorophenoxyacetic acid (2,4,5-T or Agent Orange) as a sole source of carbon at concentrations of 1 mg per gram of soil (Chatterjee et al., 1982) and 1 mg per milliliter (Kilbane et al., 1982), within one week. Optimum degradation rates occurred at 30°C and 25 percent moisture content (Chatterjee et al., 1982). Another organism, Pseudomonas diminuta, was found to have enhanced capabilities to hydrolyze parathion because of plasmid pCSI (Serdar et al., 1982). The degradation of a number of chlorinated hydrocarbons such as 3-chloro or 4-chlorobenzene has recently been reported (Kellogg et al., 1981). Kellogg et al. (1981) have demonstrated that plasmid pAC25 which encodes the complete degradation of 3-chlorobenzoate does not allow host cells to use 4-chlorobenzoate. However, the introduction of the TOL plasmid, which specifies for xylene and toluene degradation, provides the microbe with a broad substrate-specific benzoate oxygenase which allows the host cell to degrade 4-chlorobenzoate and extends the cell's metabolic range to other chlorobenzoates as well. These plasmids appear to evolve by recruitment of a variety of genes from other plasmids and interact among themselves to extend the substrate range of host cells to a wide variety of xenobiotic compounds. Kellogg et al. (1981) report having developed by plasmid assisted molecular breeding a culture of microorganisms harboring a variety of plasmids (such as CAM, TOL, SAL, pAC21 and pAC25) which were capable of degrading 2,4,5-trichloro-phenoxyacetic acid at concentrations of 1.5 to 2 mg/ml. These and similar laboratory derived microbial systems are being developed for commercial use (Doggett, 1983; Kopecky, 1983; Zitrides, 1978). These include the nine BI-CHEM systems (Kopecky, 1983), the PHENOBAC systems (Zitrides, 1978) and the strains of pseudomonads being developed by Doggett (Doggett, 1983).

2.2.4.6 Phthalate Esters

Esters of phthalic acid are industrially important chemicals used mainly in the manufacturing of plastics, pesticides, and cosmetics and are ubiquitous in the environment (Aftring, 1981; Benckiser and Ottow, 1982). Aftring et al. (1981) reported that mixed cultures of bacteria from aquatic sediments were capable of degrading phthalic acid, isophthalic acid and terephthalic acid under anaerobic conditions. Benckiser and Ottow (1982) have reported on the metabolism of di-n-butylphthalate by a denitrifying strain of Pseudomonas pseudoalcaligenes B20 bl. They suggested that one butanol moiety mostly served as the carbon source for growth and denitrification. Others have identified the mineralization of di(2-ethylhexyl) phthalate in lake water at trace concentrations (Rubin et al., 1982) and the biodegradation of this phthalic acid ester in a marine environment (Subba-Rao et al., 1982). Wolf et al. (1980) have identified second order microbial degradation rate constants for four phthalate esters obtained from sediment microorganisms and correlated them with second order alkaline hydrolysis rate constants. The plasticizer diethyl phthalate was also reported degradable by aufwuchs bacteria (microbial growth attached to submerged surfaces) (Lewis and Holm, 1981). Microbial systems reported to degrade phthalate esters have been identified in Appendix A.

2.2.4.7 Nitrosamines

Nitrosamines have received a great deal of recent attention because of their carcinogenicity, mutagenicity and teratogenicity, and their presence in foods, drugs and pesticides. These compounds have also been found in soils and water and the potential for formation in the environment has been reported (Kobayashi and Tchan, 1978; Yordy and Alexander, 1980).

In polluted waters, the compound dimethylnitrosamine has been shown to occur as a result of sludge decomposition. However, photosynthetic bacteria and other microorganisms were found to anaerobically metabolize this compound (Kobayashi and Tchan, 1978). The carcinogen n-nitrosodiethanolamine (NDEIA) was shown to degrade slowly at low concentrations (1 ug/ml) in samples of sewage and lake water under anaerobic conditions (Yordy and Alexander, 1980). The products formed appeared to be modified dimers of NDEIA and were slowly mineralized in sewage. The bacterial degradation of nitrosamines is identified in Appendix A. When provided in the literature, general environmental conditions and byproducts are identified.

2.3 Application to Waste Deposits

Commercial operations already exist (Aquifer Remediation Systems, 1985; Doggett, 1983; Flathman and Caplan, 1985; Jhaveri and Mazzacca, 1983; Kopecky, 1983; Kretschek and Krupka, 1984; Yaniga, 1982; Zitrides, 1978; USEPA, 1984) which either have microbial strains in stock capable of degrading organic wastes in situ or in portable biological reactors, and have the facilities to adapt these organisms, or native microbes, to specific waste reclamation problems. Among the companies contacted, four were willing to provide information on their products, treatment processes, and site applications and are identified by reference in this document (Jhaveri and Mazzacca, 1983; Doggett, 1983; Kopecky, 1983; Zitrides, 1978). The remaining organizations contacted considered their treatment processes or products proprietary information or simply had insufficient information on product application to be useful and therefore were not referenced in this document.

In renovating hazardous waste sites, site operators may choose to develop native populations to degrade wastes or may wish to use a commercial operation to treat a site. The information presented below was developed from case histories on treating surface soils (Doggett, 1983; Kaplan and Kaplan, 1982; Kilbane et al., 1982; Kopecky, 1983; Zitrides, 1978), deep soils and groundwaters (API, 1982; Jhaveri and Mazzacca, 1983; Kaplan and Kaplan, 1982; Zitrides, 1978), lagoons or surface impoundments (Zitrides, 1978) and industrial waste treatment plants (Zitrides, 1978).

2.3.1 Site Assessment

Before a waste site can be reclaimed, the extent and degree of contamination must be assessed as described in Chapter 1 of this report and in Repa and Kufs (1985). This includes chemical analysis to identify and quantify hazardous materials. The waste pile and soils surrounding the site should also be tested for porosity, pH, nitrogen, phosphorous and trace minerals, to establish the nutritional content of the soils and materials to be treated.

The proper microorganisms or groups of microbes must be selected to treat the waste. Commercial firms use their past experience, laboratory screening, onsite test plots, or any combination of these procedures to identify the proper agents (either native populations or constructed strains) for waste site renovation. If native microorganisms are selected, the laboratory cultivates the microbes in the presence of low waste concentrations.
The initial waste concentration used is determined by performing waste toxicity studies on the native populations. In order to breed organisms capable of degrading specific wastes or waste groups, it may be necessary to initially isolate and test individual species from the native population for their ability to degrade identified waste groups (Kellogg et al., 1981) or simply develop a waste degrading system using the entire native population (Kaplan and Kaplan, 1982). The microbes or native populations are then innoculated into laboratory scale systems that model the environment of the contaminated site with respect to soil moisture, pH, temperature and pE (dissolved oxygen content). In many instances a chemostat, fermentor or other dynamic modeling system (microcosm) can be used for this purpose (Doggett,

1983; Flathman and Caplan, 1985; Jhaveri and Mazzacca, 1983; Kaplan and Kaplan, 1982; Kellogg et al., 1981; Kopecky, 1983; Zitrides, 1978). Native microbial populations or microorganisms selected from these populations for their ability to degrade specific waste groups can then be fed increasing concentrations of the waste groups involved until a population develops that is capable of degrading the hazardous organic components at on-site concentrations under ambient environmental conditions. Laboratory studies of this nature can take up to a year or longer to complete (Kellogg et al., 1981; Jhaveri and Mazzacca, 1983).

Commercially available systems and adapted native microflora will use wastes as sole carbon sources. However, these organisms also require sources of nitrogen, phosphorus and trace elements which may not be present at the waste treatment site in sufficient concentration to support optimum growth. Generally, the desired ratio of carbon:nitrogen:phosphorus is 100:15:3. To achieve this ratio, an analysis of the site soil matrix is required. The contaminated site is modeled in the laboratory and augumented with commercially available fertilizer sources (ammonium nitrate, sodium phosphate, etc) until the desired ratio is obtained (Jhaveri and Mazzacca, 1983). Two of the firms contacted for this study (Kopecky, 1983; Zitrides, 1978) have proprietary formulations available for use as part of their treatment package, but must still determine concentrations required for optimum waste degradation by modeling the system in the laboratory. This process usually takes four to six weeks (Kopecky, 1983; Zitrides, 1978).

Site temperatures, waste type or concentration, or other environmental factors may render the waste insoluble. Emulsifying agents (surfactants) may be required to increase the microbial availability of low solubility waste constituents. Optimum treatment occurs when wastes are solubilized at a rate that will allow maximum microbial catabolic (degradation) rates under the environmental conditions imposed. If wastes are solubilized too slowly, then maximum microbial growth rates will not be achieved due to insufficient substrate concentration. If wastes are solubilized too rapidly, then microbial growth may be inhibited by excess substrate in the environment. Therefore it is important to determine, in the laboratory or in test plots at the site, the optimum concentrations of microbes, emulsifier and fertilizer required to support maximum biological activity. Two waste treatment companies (Kopecky, 1983; Zitrides, 1978) have identified emulsifiers that are available as part of their treatment packages.

Optimal microbial activity occurs in partially or fully saturated soil conditions (-0.1 to 1.0 bars soil water vapor pressure, USEPA, 1984). The degradation rates of organic compounds may thus be enhanced by addition of water (via irrigation, flooding, injection, etc. -- see Section 1.2) or drainage of saturated soils (via drainage ditches or wellpoints -- see Section 1.3).

Depending on the waste types and microbial degradation pathways to be used, aerobic or anaerobic conditions may be required (see Section 2.2). Oxygenation can be accomplished by surface filling (USEPA, 1984), injection of air (Jhaveri and Mazzacca, 1983), ozone (Nagel, 1982), or hydrogen peroxide (Wetzel et al., 1985; Aquifer Remediation Systems, 1985). Anaerobic conditions can be generated by flooding (without oxygen injection) and addition of excessive amounts of easily biodegradable organic matter (to utilize available oxygen) (USEPA, 1984). In addition, the surface may be covered with a synthetic membrane liner, compacted or temporarily sealed to reduce the influx of oxygen.

The soil or groundwater pH may also require alteration, since optimal microbial growth is in the pH range of 6-8 (Fannin et al., 1981). Soil pH is also an important factor in determining the effects of pesticides on soil microbes (USEPA, 1984). Crushed limestone, lime products, or soda ash can be used to increase the pH while acid-producing materials (aluminum or ferrous sulfate) or sulfur will lower the soil pH (USEPA, 1984).

It has been shown in extensive laboratory testing that supplemental carbon and energy sources (easily-biodegradable organic matter) can stimulate the biodegradation of recalcitrant organic compounds through cometabolism (Fogel et al., 1982; Jacobsen et al., 1980; Kaplan and Kaplan, 1982; Patil et al., 1982; USEPA, 1984 and references therein). This process has been used to promote the biodegradation of recalcitrant chlorophenol compounds at the

Picillo Farm Site, Rhode Island (see Section 2.3.5; also Flathman et al., 1983 and Flathman and Caplan, 1985). An interesting aspect of soil amendment with organic matter is the use of analog enrichment to promote cometabolism. In this approach, a non-hazardous chemical analog of the hazardous compound is added to the waste deposit to stimulate the native microbes' degradative pathways for that type of compound. The structurally-similar hazardous compound is often cometabolized (Alexander, 1981; USEPA, 1984 and references therein). For example, addition of biphenyl to test soils stimulated the biodegradation of polychlorinated biphenyls (PCBs) (Brunner et al., 1985). The potential use of non-specific organic amendments or specific chemical analogs to promote cometabolism would require evaluation during laboratory and field pilot studies.

Once the proper microbial strains, site saturation, pH and oxygen requirements, fertilizer formulations and emulsifier concentrations have been identified, and the degradation rates and application rates are known, the time course and economics of treatment can be identified for each site. Using information gained from laboratory studies, scaled-up pilot studies may be required to model waste treatment systems under field conditions to confirm technical and economic feasibility of biological waste treatment (Zitrides, 1978). This study would be most appropriate if continuous long term treatment is required. Having completed the above steps, sufficient quantities of biological agents can be cultured and freeze-dried for transport, storage and use at the site.

Based on the information developed above, the procedures to properly implement an in situ biodegradation system (Zitrides, 1978) are summarized below:

- Collect data on waste sample analysis, soil composition and indigenous microbial populations;

- Obtain monitor well data if applicable;

- Collect any other site data (soil type, moisture, pH, pE, temperature, nutrients, etc.), necessary to complete a bench-scale study;

- Analyze data and choose or breed proper microorganisms;
- Mutate and culture those microbes to perform desired functions;
- Inoculate waste samples with selected microbes under accepted scientific procedures, and observe biodegradation rates;
- Determine optimum soil moisture, pH, oxygen, fertilizer and emulsifier requirements;
- Establish technical and economic feasibility of biological approach to waste treatment;
- If technically and economically feasible, perform pilot study if required;
- Construct treatment system and begin in situ waste treatment.

2.3.2 Case Histories of In Situ Treatment of Surface Waste Deposits or Spills

2.3.2.1 Cleanup of Crude Oil Spill at an Oil Storage Site

A 1.6 hectare (four acre) spill area with crude oil penetration to a depth of 0.5 meters (1.5 feet) was restored to a condition where oil could not be detected in the soil (Zitrides, 1978; Kretschek and Krupka, 1984). The cleanup process began by flooding the spill area to float unabsorbed crude oil. Vacuum trucks removed floated oils, leaving oil residues absorbed in soil. The site was tilled to create an aerated matrix of soil and crude oil. Approximately 180 kg (400 pounds) of nutrient slurry (POLYBAC N) and 18 kg (40 pounds) of nonionic dispersant (POLYBAC E) were sprayed over the site to precondition it for optimal microbial growth. A total of 23 kg (50 pounds) of HYDROBAC bacteria (a commercially available, adapted, mutant bacterial culture) were reconstituted with 1900 liters (500 gallons) of clean water and sprayed over the contaminated area and the soils tilled again. Nutrients, emulsifier and bacteria were reapplied after six weeks; the site was tilled as required for aeration and to assure the complete mixing of microbes, fertilizers and emulsifiers with the waste materials. Soil moisture was maintained through application of water to keep the soil moist but not flooded. Following two months of treatment, the site supported vegetation and the appearance of the area was approaching normal. The treatment reduced oil concentrations in the soil by 66% during the first five weeks (Kretschek and Krupka, 1984). Treatment continued until crude oil residues could not be observed in soils.

2.3.2.2 Applications of Adapted Bacterial Cultures to Surface Waste Deposit Sites

The process of selection and application of DETOXSOL bacterial cultures for specific contamination problems involves laboratory screening, testing at onsite pilot plots and review of past experience with similar problems (Kopecky, 1983). In general, the selected bacterial culture is sprayed evenly over the site at the rate of one kilogram of bacteria per 25 m^2 (one pound of bacteria per 120 ft^2). The bacteria are applied at weeks 1, 2, 4, and 6 of the treatment period, and every two weeks thereafter as required. Soils are assayed for removal of organic contaminants before each application. The contaminated site is usually watered daily to keep soils damp but not to the point of flooding. The ground is tilled weekly when soil aeration or mixing is required.

Soils are monitored for ammonia-nitrogen and orthophosphates. If these minerals are found to be less than 5 ppm, then four kg of 8-8-8 (8% each of C, N and P) fertilizer are added per 25 m^2 (four pounds per 120 ft^2) with the bacterial application. Soils may be covered with polyethylene to stabilize temperature and moisture. This method was described as effective to depths of eight to twelve inches depending on soil porosity (Kopecky, 1983). However with extended time and by using injection wells, sites can be detoxified to depths of several feet or more. Four case histories (Kopecky, 1983) in which this system was successful in the treatment of styrene, atrizine, petroleum distillate and trichlorophenate are shown in Table 2-1.

TABLE 2-1

EXAMPLES OF BIOLOGICAL RENOVATION AT CONTAMINATED SURFACE SITES[1]

Waste Site Contaminant	Concentration (ppm)	Waste Site Characteristics	Biological Agent	Treatment Time (Days)	Residual Concentration (ppm)	Reference
Styrene	25	Railroad tankcar spill, area soils contaminated to a depth of 8 inches	BI-CHEM SUS-8	21	less than 1	1
Atrazine	Saturated Soil	50 Acre field	BI-CHEM-PBO-6			1
Sludge containing Tricholorophenate	300	Sludge spread on soil to a depth of 6 inches	BI-CHEM-GEC-1	28	less than 1	1
Petroleum Distillate	12,000	Spill covering 4 acres at an oil tank farm	BI-CHEM-SUS-8	21	less than 1	1
Acrylonitrile	1,000	Soil and groundwater Contamination	PHENOBAC	90	less than 1	2
Formaldehyde	1,400	Soil and groundwater contamination	PHENOBAC	22	less than 1	2
Ortho-Chloro-phenol	15,000	Soil and groundwater Contamination	MUTANT BACTERIA	274	less than 1	2

[1] Application of biological agents and site treatment for these examples are similar to those procedures described in the text to treat hazardous organic wastes.

References: 1) Kopecky, 1983
2) Zitrides, 1978

2.3.2.3 Biodegradation of Formaldehyde in Surface Soils

The main valve on a railroad tank car containing a 50% formaldehyde solution was inadvertently opened and about 80,000 liters of the solution spilled over the railroad ballast, into an adjacent ditch, through an orchard irrigation system and into a river (Kretschek and Krupka, 1984). The ponded formaldehyde was removed by vacuuming, and biological treatment was selected as the least disruptive and most cost-effective approach for cleaning the contaminated soil and railway ballast, which contained 700 to 1400 ppm formaldehyde. HYDROBAC bacteria, an adapted mutant culture, was tested in the laboratory (in media supplemented with soil extract and nutrients) and shown to be capable of degrading formaldehyde (Kretschek and Krupka, 1984).

A 75,000 l (20,000 gallon) bioreactor was filled with fresh water, nutrients, surfactant and bacterial innoculum (HYDROBAC) and aerated (Kretschek and Krupka, 1984). The solution from the tank was sprayed over the railroad track ballast at a rate of 190-380 l/min. Leachate was collected in a drainage ditch. The solution was continuously recycled and fresh water, nutrients, surfactants and microorganisms were added daily. During the first week of treatment, the formaldehyde concentration in the leachate was reduced from 750 ppm to 250 ppm (Kretschek and Krupka, 1984). Following three weeks of treatment, residual formaldehyde in the leachate was less than one ppm.

2.3.3 Case Histories of In Situ Treatment of Subsurface Waste Deposits or Spills

Subsurface waste deposit renovation poses problems relating to oxygen supply, temperature, permeability and accessibility (API, 1982; Kopecky, 1983; Zitrides, 1978) not encountered with surface disposal sites. Waste treatment involves pumping selected microbes, including emulsifiers, fertilizers and an oxygen source into wells penetrating the waste deposit and into peripheral or downgradient wells (API, 1982; Doggett, 1983; Jhaveri and Mazzacca, 1983; Kopecky, 1983; Zitrides, 1978) as required. Thus not only the waste pile is treated but any groundwater plumes that may be migrating from the site may be renovated as well.

Liquids recovered from the waste deposit are monitored to determine waste degradation rates and may be used in the formulation of bacteria-emulsifier and oxygen source-fertilizer preparations. Additional liquid treatment may be required and may be cost-effective at the site surface prior to its reinjection back into the waste site (Jhaveri and Mazzacca, 1983). If recovery liquid is insufficient for this purpose, it may be supplemented with fresh water. Sites low in moisture content can be moistened by the injection of fresh water along with the treatment preparations.

The practicality of subsurface waste site renovation ultimately depends on soil and waste pile permeability and site temperature. The treatment of waste sites in high clay content soils, wastes containing large concentrations of highly insoluble waste, or a combination of these factors may make biological renovation of waste sites impractical. Waste site temperatures are controlled by in situ soil temperatures and biological activity. Any environmental or biological factors which may cause a site to be too cold or too hot will adversely affect biological waste treatment. Temperatures at waste disposal sites should be high enough to support microbial growth. Low temperature has been reported as a limiting factor for microbial growth and this is reflected in the 8 to 24 month renovation time required for subsurface waste treatment using biological agents.

In addition to in situ treatment with biological agents, a water-emulsifier mixture can be pumped into the waste deposit and the waste-bearing mixture pumped to the surface and treated in a biological reactor (Jhaveri and Mazzacca, 1983; Kopecky, 1983; Switzenbaum and Jewell, 1980; Zitrides, 1978). This procedure allows for more accurate temperature and environmental control than conventional in situ treatment. Alternatively a trench or pond may be used as a biotreater (Zitrides, 1978) depending on environmental conditions, economics and geological considerations. These biotreaters may be used as either suspended microbial reactors or attached film expanded-bed reactors (Doggett, 1983; Jhaveri and Mazzacca, 1983; Kopecky, 1983; Switzenbaum and Jewell, 1980; Zitrides, 1978). The attached film process has been shown to have twice the efficiency of the suspended population system under aerobic conditions (Switzenbaum and Jewell, 1980).

Effluent from biological reactors can be polished by passage through carbon filters or adsorptive resins (such as XAD resins) if further treatment is required (Doggett, 1983). Due to the capital investment for equipment, this procedure is most economical for long term treatment of heavily contaminated areas. However, smaller portable biological reactors are also available for short term treatment of contaminated sites (Zitrides, 1978). Examples of application of biological treatment to subsurface wastes are described below.

2.3.3.1 Renovation of Groundwater and Deep Soils Contaminated by Gasoline

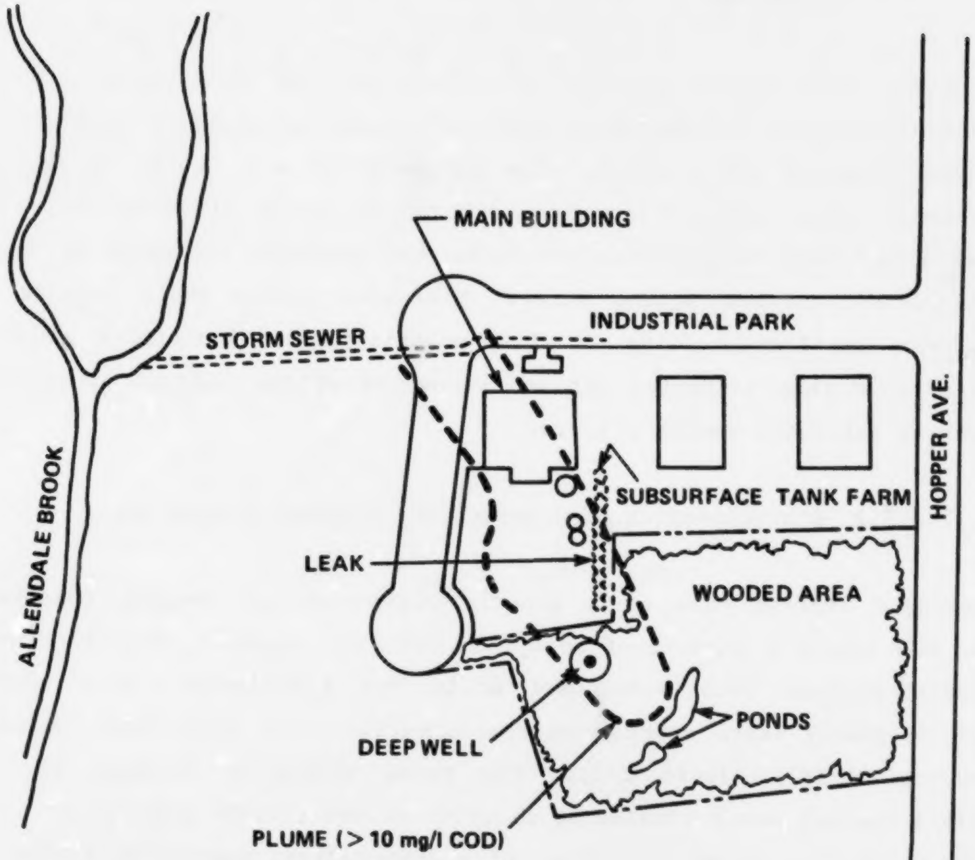
A bench scale study on the removal of leaded gasoline from subsurface soil strata and groundwater recommended a combined biological/physical treatment as the optimum approach (API, 1982). The contaminated area would be injected with nutrients and a hydrogen peroxide solution at levels above and below the water table in order to continuously bathe the gasoline contaminated region with oxygenated, nutrient-filled water. Microbial action would degrade and emulsify the gasoline, aiding in its mobilization. Emulsified gasoline byproducts could then be pumped out and renovated at the surface by physical means such as activated carbon filters.

2.3.3.2 Bioreclamation of a Subsurface Organic Solvent Spill

An underground storage tank at a generic pharmaceutical company (Biocraft, Waldwick, NJ) leaked a mixture of methylene chloride, acetone, n-butyl alcohol and dimethyl-aniline into subsurface soils and groundwater, with surface intrusion to nearby storm sewers and contamination of a local brook (Jhaveri and Mazzacca, 1983) (Figure 2-1). The total volume of leakage was not accurately known but was estimated at 113,000 liters (30,000 gallons).

A biological reactor system consisting of a downgradient dewatering trench and dewatering well system, two mobile biological activating tanks and two mobile settling tanks, and two upgradient reinjection trenches was installed. Contaminated groundwater was pumped into the bioreactors where biodegradation rates were significantly increased by supplying air and nutrients. Sludge was settled from the treated water in the settling tanks and reintroduced to the

FIGURE 2-1
BIOCRAFT SITE PLAN


MAIN BUILDING
INDUSTRIAL PARK
STORM SEWER
ALLENDALE BROOK
SUBSURFACE TANK FARM
HOPPER AVE.
LEAK
WOODED AREA
PONDS
DEEP WELL
PLUME (> 10 mg/l COD)

(SOURCE: JHAVERI AND MAZZACCA, 1983)

activating tanks. Renovated waters were discharged to the reinjection trenches. Figure 2-2 illustrates the basic process flow diagram of this system. Groundwaters were treated at the rate of 52,000 to 76,000 liters (14,000 to 20,000 gallons) per day with a median contaminant reduction of 60 percent per pass. The site operators estimate that about 40 percent of the biodegradation of wastes occurs in the deposit itself as a result of reinjection of bioactive (microbes and nutrient-supplemented) water. This treatment process is described in greater detail in Section 6.5 of this report.

An essentially similar system (with the addition of an initial air stripping step) for remediation of soil and groundwater contamination by dichlorobenzene and methylene chloride is described by Quince and Gardner (1982).

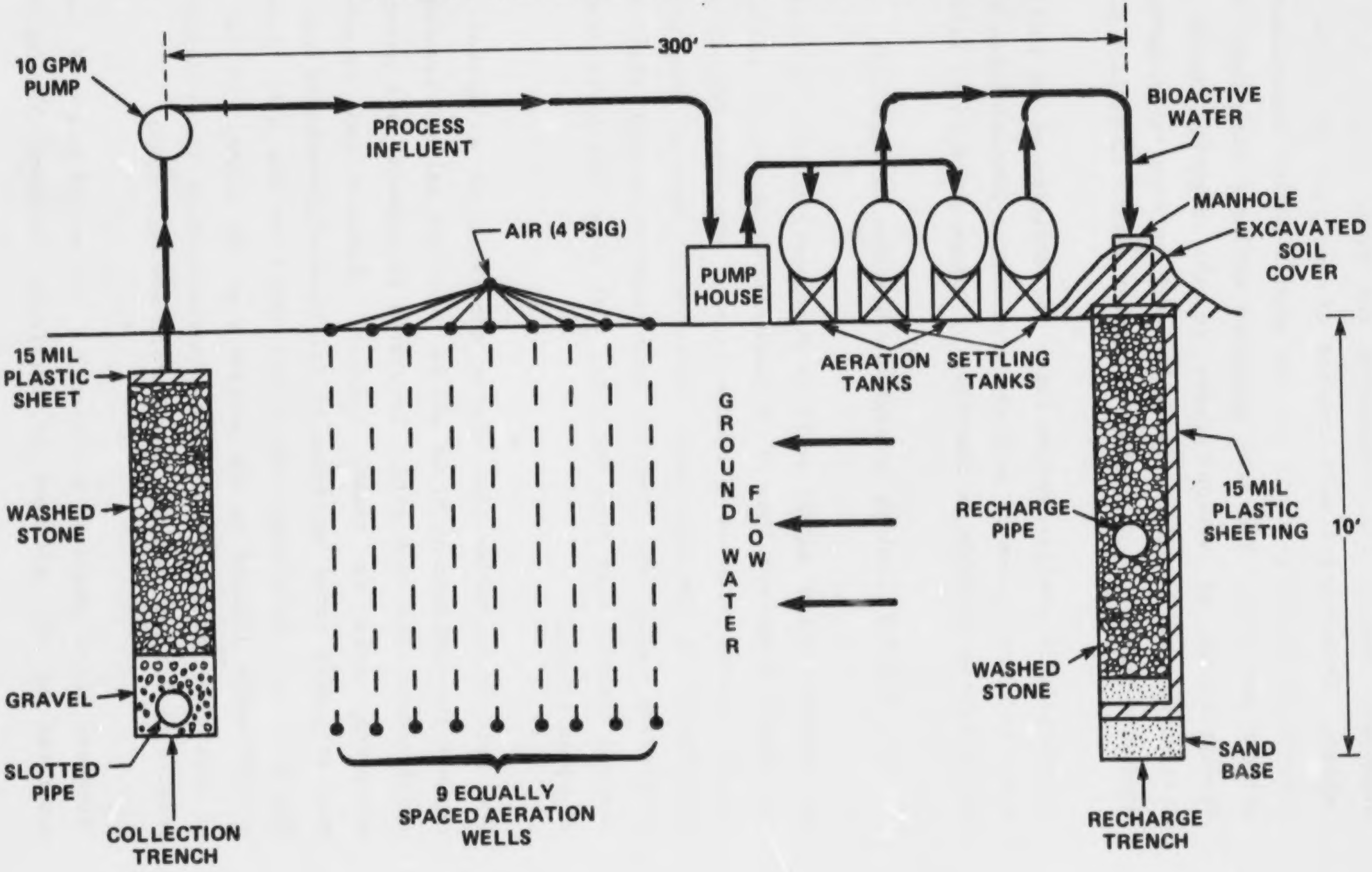
2.3.3.3 Leaking Underground Gasoline Storage Tank

Ten domestic water supply wells in Montgomery County, PA were contaminated by low level, long-term loss of an undetermined amount of gasoline from a below ground storage tank at a nearby service station (Yaniga, 1982). Soil and groundwater in the area were contaminated, but no free product was found. Monitoring wells and domestic well samples showed that a plume extended several hundred feet from the site, with dissolved hydrocarbon concentrations of up to 15 ppm.

The initial bioreclamation system consisted of a central pumping well to capture the contaminant plume and an injection gallery located at the original spill source (the tank pit). Recovered groundwater was passed through an air stripping tower to remove volatile organics and oxygenate the water. Nutrients were added batchwise to the treated groundwater and injected through the gallery. Additional oxygen was added to the site through six (6) air sparger wells located on the periphery of the plume. In the first 20 months of operation, maximum hydrocarbon concentrations in groundwater samples were reduced to 2.5 ppm (Aquifer Remediation Systems, 1985).

"Enhanced Bioreclamation" was used for the second phase of remediation. This consisted of the addition of nutrients (Restore 352 Microbial Nutrient:

FIGURE 2-2
BIOCRAFT BIODEGRADATION TREATMENT SYSTEM
BASIC PROCESS FLOW DIAGRAM


300'
10 GPM PUMP
PROCESS INFLUENT
BIOACTIVE WATER
MANHOLE
EXCAVATED SOIL COVER
AIR (4 PSIG)
PUMP HOUSE
15 MIL PLASTIC SHEET
AERATION TANKS
SETTLING TANKS
GROUND WATER FLOW
WASHED STONE
RECHARGE PIPE
15 MIL PLASTIC SHEETING
10'
GRAVEL
SLOTTED PIPE
COLLECTION TRENCH
9 EQUALLY SPACED AERATION WELLS
WASHED STONE
SAND BASE
RECHARGE TRENCH

ammonium chloride, sodium phosphate and trace elements) and an oxygen source (hydrogen peroxide) through four injection wells (Aquifer Remediation Systems, 1985).

In response to nutrient addition, there was a ten fold increase in total bacteria and a 200 fold increase in hydrocarbon degraders. Over a period of 2-1/2 months, the hydrocarbon concentration in groundwater was reduced to about 250 ppb. Activated carbon adsorption was used in the final phase to "polish" the groundwater to acceptable residual concentrations (Aquifer Remediation Systems, 1985).

2.3.3.4 Leaking Underground Storage Tanks

Vapors discovered in a laboratory building at a midwestern industrial facility were traced to leaking tanks in a below-ground tank vault for storing fuels and solvents. Free product was found to be confined to the vault area. Groundwater contamination was confined primarily to the vault, with some dissolved hydrocarbons being detected in the clay strata immediately adjacent to the tanks. Soils throughout the vault were saturated with aromatic and aliphatic hydrocarbons. Total contamination was calculated to be about 2500 liters of free product, and 1100-3400 liters of hydrocarbons adsorbed to soils (Raymond et al., 1976).

Following free product removal, bioreclamation was used to treat the contaminated soil and groundwater. Laboratory investigations verified that the site contained acclimated native bacteria capable of gasoline degradation. Thirty percent solutions of ammonium sulfate, disodium phosphate and monosodium phosphate were introduced using injection wells to provide nutrients. An average of ten aeration systems pumping at 28.3 l/min (2.5 cfm) were employed to provide oxygen. Over the next twelve months, eighty-seven tons of inorganic nutrients were introduced into the area (Raymond et al., 1976).

The introduction of nutrients lead to an average one hundred fold increase in the number of gasoline-utilizing bacteria in wells within the spill area. When nutrient addition was stopped after about one year, the water at the producing wells contained between 0-2.5 ppm of gasoline. Within six months this level dropped further, to a nondetectable level (Raymond et al., 1976).

During the project, thirty two bacterial cultures capable of degrading gasoline were isolated. Most of these isolates were unable to degrade many of the individual components of gasoline. This suggests that significant cometabolism occurs in the subsurface environment. The cultures were identified as primarily Norcardia, Pseudomonas and Acinetobacter (Raymond et al., 1976).

2.3.3.5 Bioremediation of Groundwater Contaminated with Fuel Oil and Solvents

Groundwater contamination by fuel oil, benzene, xylene, toluene, naphthalene and styrene was discovered on an industrial site near Frankenthal, West Germany. After recovery of free fuel oil, it was estimated 20 to 30 metric tons of adsorbed and dissolved hydrocarbons remained in the ground (Stief, 1984). Combined hydraulic flushing and induced biodegradation was used to treat this residual contamination.

The local water authority required that nutrients injected into the aquifer to accelerate biodegradation and the flushed contaminants be kept within a defined area so that the surrounding aquifer was not contaminated. Two separate recirculation lines were installed, one for the flushing water (5 l/sec) and the second for clean injection water (20 to 30 l/sec). The recirculated flushing water, contaminated with hydrocarbons and biodegradation by-products, was stripped and filtered before re-infiltration. Biodegradation was enhanced by controlling the dosage of the nutrient nitrate and by increasing the water temperature 10°C (Stief, 1984).

Biodegradation of aromatic hydrocarbons was simpler than degradation of aliphatic hydrocarbons, and benzene biodegradation was better than that of xylene and toulene. After three months it was found that aromatics had been degraded in the whole area, and aliphatics were reduced to about one-third of their initial concentration (Stief, 1984).

2.3.3.6 Biodegradation of Ethylene Glycol in Groundwater

Approximtely 15,000 liters (4000 gallons) of 25% ethylene glycol solution leaked from a storage lagoon at the Naval Air Engineering Center, Lakehurst, NJ, contaminating the soil around the lagoon and creating a downgradient plume (Flathman et al., 1984; Flathman and Caplan, 1985). A feasibility study showed that the environment was not toxic to the native microfauna, which were already adapted to and biodegrading the ethylene glycol in situ, although pH and nutrient adjustment would be necessary to optimize bacterial degradation rates (Flathman et al, 1984; Flathman and Caplan, 1985).

The biotreatment system included:

1) a series of injection well points (1.5 m spacing, 5 m deep) to inoculate the soil and groundwater with adapted indigenous microbes and nutrients (inorganic nitrogen and phosphorus) and adjust the pH;

2) five recovery wells to withdraw contaminated groundwater from beneath the lagoon and from the plume; and

3) a surface aerator/bioreactor (activated sludge system) to further treat the recovered groundwater.

Surface application was also used to flush ethylene glycol from the unsaturated zone in the soil. Biodegradation of the ethylene glycol took place both in situ and in the reactor (Flathman et al., 1984).

During the initial treatment period (26 days), groundwater concentrations of ethylene glycol were reduced by 85-93% (Flathman et al., 1984). The subsequent maintenance program focused on removal of the remaining pockets of contamination by continued surface application of lime (to raise the pH) and nutrients which are washed into the soil by natural precipitation (Flathman et al., 1984).

Two interesting observations can be made regarding this remedial process:

1) Natural (adapted) microfauna were used to accomplish the biodegradation; augmentation with commercial strains was not required.

2) Ethylene glycol held in the unsaturated zone by capillary action was aggressively flushed during the treatment process and biodegraded, along with that in the groundwater.

2.3.4 Liquid Surface Waste Deposits

Lagoons, ponds and industrial waste treatment plants are amenable to renovation using biological treatment. In essence, the entire water body becomes a biological reactor. Optimum concentrations of bacteria, emulsifiers and fertilizers are introduced and maintained in these systems until renovation is complete. These surface waters can be monitored daily for biological oxygen demand (BOD) reductions, which indicates the progress in degradation of the catabolizable organics present. Renovation times for ponds or lagoons containing high BOD levels range from 3 to 12 months depending on the level of contamination (Zitrides, 1978). Unlike ponds, industrial treatment plants are usually designed as flow-through chemostats in which high concentrations of organic waste mixtures can be treated on a continual basis. Treatment of waste streams in excess of 500,000 mg/l BOD have been reported (Zitrides, 1978).

A lagoon containing 500,000 ppm waste oil and grease (floating, dispersed and deposited as sludge) in 15,000 m^3 (four million gallons) of liquid was treated by biological degradation (Zitrides, 1978). This system was inoculated with 68 kg (150 pounds) of PETROBAC, 68 kg (150 pounds) of PHENOBAC, micronutrients (POLYBAC N) and emulsifiers (POLYBAC E). Ongoing treatment consisted of regular addition of bacteria, nutrients and emulsifiers. Freezing temperatures forced the shutdown of pumps and compressors that served to aerate the system during the winter. Treatment was resumed in a second phase using the procedures described above.

High biological activity was observed within four weeks of initial treatment. The bacteria were able to degrade 99 percent of the waste oil within seven months of initial startup. Lagoon wastewaters, after renovation, were discharged to local sewers at the rate of 75 m^3 (20,000 gallons) per day with no adverse effect on the municipal trickling filter system.

2.3.5 Renovation of Waste Disposal Sites

Only one practical example was found in the literature on the use of biological agents for in situ renovation of sites at which chemical wastes were intentionally disposed (Flathman et al., 1983). The use of native (Mancinelli et al., 1981) or naturally adapted (Kellogg et al., 1981) microorganisms for waste disposal site renovation has also been suggested in the literature, and a number of significant advances have been made in the last five years on in situ biological treatment methods for hazardous waste. The most promising in situ approach is the work of Kellogg et al. (1981) and others (Rosenberg and Alexander, 1979; Schwien and Schmidt, 1982; Serdar et al., 1982) using constructed strains of microbes. Proprietary systems (Aquifer Remediation Systems, 1985; Doggett, 1983; Jhaveri and Mazzacca, 1983; Kopecky, 1983; Zitrides, 1978) are assumed to be derived by similar but not necessarily identical mechanisms of selection and adaption as those previously described (Kellogg et al., 1981; Perry, 1979; Schwein and Schmidt, 1982; Serdar et al., 1982).

2.3.5.1 Biodegradation of Phenolic Compounds in Contaminated Soils

An explosion and fire led to the discovery in 1977 of approximately 10,000 buried drums of hazardous wastes at Picillo Farm, Coventry, Rhode Island. The initial remedial measure at this Superfund site was the excavation and removal of these drums; this left approximately 1300 m^3 (46,000 ft^3) of phenol-contaminated soils, containing approximately 770 kg (1700 lbs) of phenolic compounds (Flathman et al., 1983; Flathman and Caplan, 1985).

A feasibility study indicated that the soil contained native microbes capable of degrading the phenolics (Flathman et al., 1983; Flathman and Caplan, 1985). The biotreatment system designed for the site consisted of a 0.28 hectare (0.69 acre) secure cell (land farm) draining to a 190,000 liter (50,000 gallons) bioreactor which collected and treated leachate for recirculation through a perforated pipe delivery system. The area was tilled to a depth of 46 cm (1.5 ft) to aerate the soil, and moisture content was maintained by irrigation through the perforated pipe. A mixture of commercial bacterial strains (160 kg or 350 pounds) was seeded into the soil to augment the native microbial population and pH and nutrient content adjusted as required (Flathman et al., 1983).

During the first two weeks of treatment the average total recoverable phenols concentration dropped at a rate of 150 ppm per week (Flathman et al., 1983; Flathman and Caplan, 1985). Over the next four weeks, however, the concentration dropped at a rate of only 4 ppm/week as the more readily biodegradable phenolics were destroyed, leaving more refractory phenolic compounds. At week 6 a cosubstrate (supplementary energy source) was added to increase microbial population and activity. This led to an increase in the rate of phenol destruction, to about 25 ppm/week (Flathman et al., 1983; Flathman and Caplan, 1985). By day 304 of the treatment process, the average total recoverable phenol concentration was 61 ppm, more than an order of magnitude, lower than the initial concentration and within the 100 ppm goal of the project (Flathman et al., 1983; Flathman and Caplan, 1985).

2.4 Summary

The use of biological agents for the treatment of hazardous organic wastes is a relatively new concept and is creating a biological technology for the large scale treatment of such materials (Aquifer Remediation Systems, 1985; Doggett, 1983; Flathman et al., 1983; Jhaveri and Mazzacca, 1983; Kellogg, 1981; Kopecky, 1983; Zitrides, 1978). As in all new applications, more information concerning the use of appropriate microorganisms and the pathways that they use to degrade specific compounds will be needed before the full extent of their usefulness can be known. This will require major advances in the understanding of the genetic structure of many microbes and the creation of additional strains that can function in existing waste treatment systems or at disposal sites.

A variety of microbiological methodologies have been developed to treat sites contaminated by organic materials. Site characteristics dictate the appropriate treatment technology applicable to site renovation. These technologies have been described above, with case histories identified in Table 2-1. These technologies are summarized in Table 2-2 and are briefly reviewed below. Organic waste sources that can be metabolized by microorganisms are identified in Table 2-3.

Reclamation of surface waste spills or piles may involve the use of native bacteria if contaminant compounds are nonhalogenated acyclic or simple unsubstituted aromatics, or low concentrations of halogenated compounds. More complex and/or halogenated compounds may require the use of adapted, mutated, plasmid assisted or constructed bacteria plus fertilizer and emulsifiers to renovate surface soils. Optimum conditions are aerobic, moist environments with a pH between 5 to 7. Anaerobic microenvironments may be required for reductive dehalogenation. Average renovation times are one to three months.

Treatment of deep soils, subsurface waste deposits and groundwater involves the stimulation of native microbes or the injection of adapted or genetically constructed bacteria with fertilizers, emulsifiers and an oxygen source directly into and around the contaminated zone. Based on the studies and case histories identified above and the commercial systems presently in use (Aquifer Remediation Systems, 1985; Doggett, 1983; Jhaveri and Mazzacca, 1983; Kopecky, 1983; Zitrides, 1978), biological systems to treat various organic contaminants present in hazardous waste deposits may now exist, and the methodology for breeding specific cultures that can degrade persistent compounds has been developed (Doggett, 1983; Kellogg, 1981; Kobayashi and Rittman, 1982; Kopecky, 1983; Rosenberg and Alexander, 1979; Schwein and Schmidt, 1981; Serdar et al., 1982; Zitrides, 1978). Applications to specific waste sites will involve the ability to control temperature, pH, dissolved

TABLE 2-2

SUMMARY OF MICROBIOLOGICAL TREATMENT TECHNOLOGIES[1]

Treatment Method

Contamination Zone	Native Bacteria	Adapted Native Bacteria	Mutant Bacteria	Plasmid Associated Bacteria	Constructed Breeding	Bioreactors	Aerobic/ Anaerobic
Waste Disposal Sites	-	±	±	+?	+?	±	+/+
Surface Waste Piles or Deposits	±	+	+	+	+	-	+/?
Subsurface Waste Deposits	-	+	+	+	+	±	+/-
Groundwater	-	+	+	+	+	+	+/-
Surface Liquid Waste Deposits	±	+	+	+	+	+	+/+

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[1] Information concerning the degradation of specific waste groups or organic species and the microorganisms degrading those materials are cited by reference in Appendix A.

"+": Technology is available

"-": Technology is not available

"?": Technology may be developed in laboratory

TABLE 2-3

SUMMARY OF ORGANIC GROUPS SUBJECT TO MICROBIOLOGICAL METABOLISM[1]

MODES OF MICROIAL METABOLISM

SUBSTRATE COMPOUNDS	Respiration					RING Fission								
	Aerobic	Anaerobic	Fermentation	Oxidation	Co-oxidation	Oxidative	Reductive	Dehalogenation	Esterification	Esterases	Dehydrogenation	Deamination	Photometabolism	Degradation
Straight Chain Alkanes	+	+	+	+	+				+		+			
Branched Alkanes	+	+	+	+	+						+			
Saturated Alkyl Halides		+		+	+			+						
Unsaturated Alkyl Halides		+		+				+						
Esters, Glycols, Epoxides	+	+	+	+							+			
Alcohols	+	+		+										
Aldehydes, Ketones	+	+		+										
Carboxylic Acids	+	+		+										+
Amides	+	+												+
Esters	+	+								+				+
Nitriles	+	+												+
Amines	+	+										+		+
Phthalate Esters	+	+		+						+				
Nitrosamines		+										+		+
Thiols														+
Cyclic Alkanes	+		+	+	+									
Unhalogenated Aromatics	+	+		+		+	+						+	+
Halogenated Aromatics	+	+		+	+	+	+						+	+

TABLE 2-3 (Continued)

SUMMARY OF ORGANIC GROUPS SUBJECT TO MICROBIOLOGICAL METABOLISM[1]

MODES OF MICROIAL METABOLISM

	Respiration					Ring Fission								
SUBSTRATE COMPOUNDS	Aerobic	Anaerobic	Fermentation	Oxidation	Co-oxidation	Oxidative	Reductive	Dehalogenation	Esterification	Esterases	Dehydrogenation	Deamination	Photometabolism	Degradation
Simple Aromatic Nitro Compounds	+	+				+	+							+
Aromatic Nitro Compounds With Other Functional Groups	+	+			+	+	+	+						+
Phenols	+	+	+	+	+	+	+							+
Halogenated Side Chain Aromatics	+		+	+		+		+						+
Fused Ring Hydroxy Compounds	+													+
Nitrophenols		+												+
Halogenated Phenols	+			+		+		+						+
Phenols - Dihydrides, Polyhydrides	+			+	+	+								+
Two & Three Ring Fused Polycyclic Hydrocarbons	+			+		+		+						+
Biphenyls	+					+								+
Chlorinated Biphenyls	+					+		+						+
Polychlorinated Biphenyls	+					+			+					+
Four Ring Fused Polycyclic Hydrocarbons	+													+
Five Ring Fused Polycyclic Hydrocarbons	+													+

TABLE 2-3 (Continued)

SUMMARY OF ORGANIC GROUPS SUBJECT TO MICROBIOLOGICAL METABOLISM[1]

MODES OF MICROIAL METABOLISM

SUBSTRATE COMPOUNDS	Respiration					Ring Fission								
	Aerobic	Anaerobic	Fermentation	Oxidation	Co-oxidation	Oxidative	Reductive	Dehalogenation	Esterification	Esterases	Dehydrogenation	Deamination	Photometabolism	Degradation
Fused Polycyclic Hydrocarbons	+													+
Organophosphates	+	+					+							+
Pesticides and Herbicides	+	+			+			+						+

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[1] This table is a condensed version of Appendix A. Please refer to the Appendix for specific organics and the biological agents participating in the metabolism of these compounds.

oxygen, moisture, nutrients, solubility of waste materials, and microbial predation. Current technology may be applied to the in situ treatment of wastes in a manner similar to that of Jhaveri and Mazzacca (1983) and Flathman et al. (1983). Additional advances may include the breeding of microorganisms with laboratory evolved plasmids capable of degrading a variety of xenobiotic compounds (Kellogg et al., 1981). Mobilized waste could be pumped to the surface from perimeter wells (API, 1982) for treatment in bioreactors (Jhaveri and Mazzacca, 1983) prior to final renovation by activated carbon or ionic filters (API, 1982; Aquifer Remediation Systems, 1985: Doggett, 1983). The range of delivery/recovery systems applicable to various waste deposit settings is discussed in Section 1.

Process applications may require several years. In cases where biological treatment cannot produce complete treatment, its use in conjunction with chemical and physical treatments may be preferable to using any one technology alone.

Renovating liquid waste deposit sites primarily involves the use of adapted, mutant, plasmid assisted or genetically constructed bacteria in conjunction with fertilizer application and aeration. Systems may be microaerophillic to anaerobic upon diffusion into soils. Average renovation times are three months to a year.

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SECTION 3

SURFACTANT - ASSISTED FLUSHING

3.1 Introduction

Flushing or mobilization of wastes can serve two purposes: to promote the recovery of wastes from the subsurface for treatment at the surface, or to solubilize adsorbed compounds in order to enhance the rate of other in situ treatment techniques (such as biodegradation or hydrolysis). Flushing or mobilization using water alone may be sufficient for relatively soluble compounds such as phenols; however, the use of chemicals such as surfactants will be required for significant solubilization of insoluble (hydrophobic) compounds. In addition, acid solutions can be used to mobilize certain organics (amines, ethers, anilines) and basic solutions can mobilize some phenols, chelating and complexing agents (USEPA, 1982).

Surfactants (surface active agents) are a class of natural and synthetic chemicals whose abilities to promote the wetting, solubilization, and emulsification of various types of organic chemicals have found widespread application. These properties make surfactants of possible use in the in situ treatment of certain organic fractions in waste deposits. Used in conjunction with various groundwater flooding and dewatering techniques, surfactants may offer a means of improving the removal efficiency of these organics over the results likely to be obtained with water alone.

An evaluation has been made of the feasibility of using surfactants for in situ waste treatment processes. Since very little information exists on the use of surfactants at waste sites, this evaluation has focused on a review of the available literature on the application of surfactants to subsoil systems and a consideration of fundamental chemical characteristics of the principal surfactant classes with respect to their applicability to in situ organic waste treatment.

3.2 Background and Theory

Surfactants are a general class of chemicals whose amphipathetic molecular structures generally consist of a hydrophobic group which has little affinity for the solvent phase (water) and a hydrophilic group which is readily soluble in the solvent phase (Shaw, 1976). The terms lyophobic and lyophilic are applied to systems where the carrier solvent is not water. This characteristic of surfactants results in their tendency to concentrate preferentially at phase interfaces (liquid-liquid, liquid-solid, liquid-gas) and is responsible for their unique abilities to alter certain properties of aqueous solutions. Surfactants might be used to enhance the effectiveness of in situ treatment technologies by improving both the detergency of aqueous solutions applied to waste deposits and the efficiency with which organics may be transported by aqueous solutions from the subsurface waste deposit to the surface.

Surfactants can increase the detergency ("cleaning power") of aqueous solutions through a number of processes. These include the following:

- Preferential Wetting - Surfactants can improve the ability of an aqueous solution to wet a solid surface (such as soil particles) by decreasing the interfacial tension between the aqueous phase and the solid phase (Rosen, 1978). By preferentially wetting the solid surface, an aqueous solution can partially or completely displace an adsorbed organic fraction. This reduction in the "strength" with which an organic fraction adheres to soil particles may enhance the effectiveness of contaminant recovery during groundwater pumping and dewatering operations.

- Solubilization - The addition of surfactants can enhance the ability of aqueous solutions to solubilize organic compounds. Solubilization results from the interaction of the amphipathetic surfactant molecules with molecules of the organic fraction. In practice, significant solubilization of organic material generally requires relatively high surfactant concentrations (above the "critical micelle concentration") which lead to the formation of surfactant micelles in the solution (Mukerjee, 1979). Micelles are discrete clusters of surfactant molecules within an aqueous phase in which the surfactant hydrophobic groups are directed toward the interior of the micelle and hydrophilic groups toward the surrounding solvent (water). Micelles can effectively incorporate or "solubilize" susceptible organic compounds either within their interiors (hydrophobic regions) or at their external peripheries (hydrophilic regions).

- Emulsification - Surfactants can enhance the detergency of an aqueous solution by promoting the dispersion of an insoluble organic phase within the aqueous phase (emulsification). Emulsion formation generally requires some minimal source of mechanical energy input. As such, emulsification processes suffer the disadvantage of often being readily reversible. Thus in a waste deposit spontaneous separation of emulsified phases may occur prior to removal of the emulsion.

3.3 Surfactant Chemical Characteristics

Surfactants are generally classified on the basis of the chemical characteristics of the hydrophilic groups. The principal surfactant classes (Rosen, 1978) are described below:

- Anionic - The surface active portion of the surfactant molecule bears a negative charge, for example $RC_6H_4SO_3^-Na^+$ (a sodium alkylbenzene sulfonate). Anionic surfactants find widespread use as detergents and wetting agents, and are the largest surfactant class in terms of usage and importance. Most groups of anionic surfactants display limited to good water solubility.

- Cationic - The surface active portion of the surfactant molecule bears a positive charge, for example, $RNH_3^+Cl^-$(salt of a long chain amine). This is a relatively small surfactant class, many of whose members find somewhat specialized uses requiring surface adsorption and surface coating.

- Nonionic - The surface active portion of the surfactant molecule does not bear apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of a long chain fatty acid). Nonionic surfactants are the second most important class in terms of use. They do not display charge effects, are generally soluble in water, and many nonionics are soluble in organic solvents.

- Amphoteric - Both positive and negative charges may be present in surface active portion of the molecule, for example, $R^+NH_2CH_2COO^-$ (a long chain amino acid). This is a small surfactant class used in situations where specialized charge properties are required.

The hydrophobic portion of surfactant molecules is typically comprised of a long chain hydrocarbon residue. Common surfactant hydrophobic groups include:

- Branched chain, long alkyl groups (C_8 - C_{20}),
- Long-chain (C_8 - C_{15}) alkybenzene residues,
- Alkylnaphthalene residues (C_3 and greater-length alkyl groups),
- Rosin derivatives,
- High-molecular weight ethylene oxide and propylene oxide polymers,
- Long chain perfluoroalkyl groups, and,
- Polysiloxane groups.

Table 3-1 provides general information on the four major surfactant types and their principal classes.

TABLE 3-1

SURFACTANT CHARACTERISTICS

SURFACTANT TYPE AND CLASSES	SELECTED PROPERTIES AND USES(1)	SOLUBILITY	REACTIVITY
ANIONIC			
1) Carboxlic Acid Salts	Good Detergency (1, 2, 3, 4, 5)	Generally Water Soluble (1, 2, 3, 4, 5)	Electrolyte Tolerant (2, 3, 4, 5)
2) Sulfuric Acid Ester Salts	Good Wetting Agents (1, 2, 3, 4, 5)	Soluble in Polar Organics (5)	Electrolyte Sensitive (1)
3) Phosphoric & Polyphosphoric Acid Esters	Strong Surface Tension Reducers (4,5)		Resistant to Biodegradation (4,5)
4) Perfluorinated Anionics	Good Oil In Water Emulsifiers - (5)		High Chemical Stability (4)
5) Sulfonic Acid Salts.			Resistant to Acid and Alkaline Hydrolysis (3, 4, 5)
CATIONIC			
1) Long Chain Amines	Emulsifying Agents (1, 3, 4)	Low or Varying Water Solubility (1, 2, 4)	Acid Stable (1, 3)
2) Diamines & Polyamines	Corrosion Inhibitor (1)	Water Soluble (3)	Surface Adsorption to Silicaceous Materials (2)
3) Quaternary Ammonium Salts			
4) Polyoxyethylenated Long Chain Amines			

TABLE 3-1 (Cont'd)

SURFACTANT CHARACTERISTICS

SURFACTANT TYPE AND CLASSES	SELECTED PROPERTIES AND USES(1)	SOLUBILITY	REACTIVITY
NONIONIC			
1) Polyoxyethylenated Alkylphenols Alkylphenol Ethoxylates	Emulsifying Agents (1, 5)	Generally Water Soluble	Good Chemical Stability (1, 6)
2) Polyoxyethylenated Straight Chain Alcohols & Alcohol Ethoxylates	Detergents (1, 2, 4, 6)	Water Insoluble Formulations (1, 6, 7)	Resistant to Biodegradation (1)
3) Polyoxyethylenated Poly-oxypropylene Glycols	Wetting Agents (2, 7)		Relatively Non-Toxic (all)
4) Polyoxyethylenated Mercaptans	Dispersents (3)		Subject to Acid and Alkaline Hydrolysis (3, 6, 7)
5) Long-Chain Carboxylic Acid Esters	Foam Control (3)		
6) Alkylolamine "Condensates", Alkanolamides			
7) Tertiary Acetylenic Glycols			
AMPHOTERICS			
1) pH Sensitive	Solublizing Agents	Varied (pH dependent)	Non-Toxic
2) pH Insensitive	Wetting Agents		Electrolyte Tolerant
			Adsorption to Negatively Charged Surfaces

(1) Numbers refer to applicable classes within a given surfactant type

One of the most important properties of surfactant solutions with respect to waste treatment lies in their ability to reduce organic/water interfacial tensions (thereby potentially enhancing wetting, emulsification and transport of organics). Unfortunately, interfacial tension data have been determined for relatively few of the specific aqueous/organic systems of potential interest with respect to waste treatment.

A simple approach to evaluating the potential use of surfactants in organic waste recovery involves consideration of the aqueous solubility of the organic phase. The aqueous solubilities of selected organic compounds of interest are listed in Table 3-2. In addition, selected octanol/water partition coefficient values (K_{ow}), which are commonly used as relative measures of the tendency of organic compounds to adsorb to soil particles (Wasik et al., 1981; Karickhoff et al., 1979) are also listed. These data demonstrate the wide ranges in water solubilities (and soil adsorptivity) possessed by potential organic constituents of waste deposits. In general, surfactants would be most effective in promoting the mobilization of organic compounds of relatively low water solubility and high log K_{ow} values. Conversely, surfactants may be of more limited value for mobilizing relatively water soluble substances.

General prerequisites for effective lowering of the interfacial tension between aqueous and organic phases by a surfactant include:

- Spontaneous surfactant adsorption at the interface,
- Molecular interaction between the hydrophobic portion of the surfactant and the organic phase, and
- Strong molecular interaction between the hydrophilic portion of the surfactant molecule and the aqueous phase.

TABLE 3 2

PROPERTIES OF SELECTED ORGANIC COMPOUNDS WHICH INDICATE THE POTENTIAL EFFECTIVENESS OF SURFACTANTS[1]

CONTAMINANT CLASS	COMPOUND	WATER SOLUBILITY (M)	OCTANOL WATER PARTITION COEFFICIENT (log K_{OW})	INTERFACIAL TENSION (Y)[2] (dynes/cm)
Normal Hydrocarbons	n-Pentane	5.65×10^{-4}	3.62	-
	n-Hexane	1.43×10^{-4}	4.11	50.0
	n-Heptane	3.57×10^{-4}	4.66	-
	n-Octane	9.66×10^{-4}	5.18	50.8
Unsaturated Hydrocarbons	1-Hexene	8.38×10^{-4}	3.47	-
	1-Heptene	1.85×10^{-4}	3.99	-
	1-Octene	3.65×10^{-5}	4.88	-
	1-Nonene	8.85×10^{-6}	5.35	-
	1-Pentyne	1.54×10^{-2}	2.12	-
Halogenated Hydrocarbons	1-Chlorobutane	9.43×10^{-3}	2.55	-
	1-Chloroheptane	1.01×10^{-4}	4.15	-
	Trichloroethylene	1.04×10^{-2}	2.53	-
	Trichloroethylene	3.2×10^{-2}*	-	37.4
	Carbon Tetrachloride	5.2×10^{-4}*	-	45.0
Ethers	Diisopropyl Ether	8.8×10^{-2}*	-	17.9
	Ethyl Ether	9.3×10^{-1}*	-	10.7
Aldehydes and Ketones	2-Butanone	1.89	0.69	-
	3-Pentanone	0.53	0.99	-
	2-Heptanone	3.57×10^{-2}	1.98	-
	2-Octanone	8.85×10^{-3}	2.76	-
	Heptaldehyde	-	-	13.7
	Methyl n-Butyl Ketone	1.7*	-	9.7
	Methyl Ethyl Ketone	4.9*	-	3.0

TABLE 3-2 (Cont'd)

CONTAMINANT CLASS	COMPOUND	WATER SOLUBILITY (M)	OCTANOL WATER PARTITION COEFFICIENT (log K_{ow})	INTERFACIAL TENSION (Y)[2] (dynes/cm)
Esters	Methyl-nonanoate	1.33×10^{-4}	4.32	-
	Methyl Decanoate	2.05×10^{-5}	4.41	-
	Ethyl Acetate	0.726	0.68	6.8
	n-Butyl Acetate	5.77×10^{-2}	1.82	14.5
Alcohols	1-Butanol	0.854	0.78	-
	1-Pentanol	0.133	1.53	-
	1-Hexanol	4.14×10^{-2}	2.03	-
	1-Heptanol	1.13×10^{-2}	2.57	-
	Octanol	2.0×10^{-3}*	-	8.5
Carboxylic Acids	Heptylic Acid	1.8×10^{-2}*	-	7.7
Aromatic Hydrocarbons	Toluene	6.28×10^{-3}	2.65	36.1
	Ethylbenzene	1.76×10^{-3}	3.13	-
	o-Xylene	2.08×10^{-3}	3.13	-
	n-Butylbenzene	1.03×10^{-4}	4.28	-
	Benzene	2.2×10^{-2}	2.13	33.9
	m-Cresol	2.59×10^{-2}*	1.96	-
Phenols	Phenol	0.81	1.45	-
	2,6-Dimethylphenol	7.90×10^{-2}	2.31	-
Halogenated Phenols	m-Cresol	2.59×10^{-3}	1.96	-
Halogenated Aromatics	Bromobenzene	2.62×10^{-3}	2.98	36.5
	o-Dichlorobenzene	6.7×10^{-4}*	3.38	-

TABLE 3-2 (Cont'd)

CONTAMINANT CLASS	COMPOUND	WATER SOLUBILITY (M)	OCTANOL WATER PARTITION COEFFICIENT (log K_{ow})	INTERFACIAL TENSION (Y)^{2} (dynes/cm)
Fused Polycyclic Hydrocarbons	Napthalene	2.39×10^{-4}	3.35	-
	1-Methylnaphthalene	2.23×10^{-4}	-	-
Amines	Aniline	3.6×10^{-2}*	-	5.8

1 Source - experimental data presented by Wasik et al. (1981) and Grain (1982)

2 In water at 20-25°C

* Values approximated from data of Verscheuren (1977) (T=20°C)

Little comprehensive, quantitative data is currently available on the relative effectiveness and efficiency with which different surfactants reduce the interfacial tensions of different aqueous-organic systems. In general, within a given surfactant class the efficiency with which a surfactant reduces the interfacial tension of a water/organic system has been reported (Rosen, 1978) to:

- increase with increasing carbon number for straight chain surfactant hydrophobic groups
- increase with the addition of phenyl groups, and
- increase less with branched chains than with straight chains of the same carbon number.

The efficiency of polyoxyethylenated nonionic surfactants generally decreases slowly with increasing oxyethylene content of the surfactant molecule.

3.4 Surfactant Application to Subsurface Deposits: Existing Information on Surfactant Behavior

A review of the literature did not reveal much information on the use of surfactants for the in situ treatment of organic waste deposits. The most comprehensive evaluation of the potential use of surfactants for the subsurface recovery of organic compounds has been in conjunction with tertiary oil recovery technologies. In addition, several laboratory studies have evaluated the feasibility of enhancing the recovery of spilled petroleum products in groundwater systems by using surfactants.

3.4.1 Tertiary Oil Recovery

The feasibility of utilizing surfactants to enhance the relatively poor recovery efficiencies obtained in tertiary oil recovery by water flooding have been studied extensively (Shah, 1977; Morgan et al., 1979). Research to date has focused on chemical characterization of those surfactants capable of generating the "ultra low" interfacial tensions (less than 0.1 dynes/cm) which calculations indicate are required for significant increases in oil recovery efficiencies under the pressurized flooding conditions attainable in well fields.

A variety of studies (Doe et al., 1977; Cayias et al., 1977; Wilson and Brandner, 1977) have demonstrated that certain sulfonates and petroleum sulfonate mixtures are particularly effective in reducing the interfacial tensions of aqueous/oil systems to very low values (10^{-2} to 10^{-4} dynes/cm). These studies and others (Cash et al., 1977; Barakat et al., 1983; Morgan et al., 1979) have shown that the extent of interfacial tension reduction in these sulfonate systems (and by analogy, possibly other surfactant classes) is affected by a variety of physical/chemical factors including the composition of the oil phase, the structure and concentration of the surfactant, the solution electrolyte concentration, temperature, pH and the molecular weight, structure and concentration of any surfactant solubilizing additives (organic alcohols). In general it has been found that significant interfacial tension reduction is observed at only a specific surfactant concentration (or within a very narrow range of concentrations). Data indicate that maximum interfacial tension reduction is observed only when the surfactant chemical characteristics (equivalent weight and structure) are closely correlated to those of the oil phase, and only for surfactant concentrations at or in excess of the critical micelle concentrations. Decreases in surfactant concentrations below critical micelle concentration values lead to abrupt increases in interfacial tension. In addition, interfacial tension has been shown to be highly sensitive to electrolyte concentrations, with both insufficient and excessive electrolyte concentrations decreasing surfactant effectiveness.

3.4.2 Petroleum Spills

The feasibility of using surfactants to recover spilled petroleum products has been studied by the Texas Research Institute (1979). In these studies the ability of a series of commercial surfactants to enhance the displacement and recovery of gasoline was evaluated in laboratory simulations of subsurface spills. Significant reductions in interfacial tension at the gasoline/water interface were considered to be a prerequisite of potential surfactant effectiveness as an agent to displace gasoline. Selected results of these studies are summarized in Table 3-3. The results indicate that the magnitude of the gasoline/water interfacial tension reduction was greater for anionic and nonionic surfactants than for fluorocarbons. However, within each class significant variations in interfacial tension were observed depending upon the specific surfactant employed.

Several surfactants which demonstrated significant interfacial tension reductions were tested for their ability to enhance gasoline displacement from laboratory sand systems after initial water flushing. Only one of the surfactants tested (Richonate YLA, an alkylaryl sulfonate) measurably increased gasoline recovery. Significantly, this was not the surfactant which had displayed the greatest reduction in interfacial tension. In addition, poor recovery flow rates were observed for this surfactant. The experiments suggested that this was caused by the formation of a viscous emulsion of surfactant solution and gasoline. Recoveries were improved (up to 40%) by the use of a mixture of anionic Richonate YLA and nonionic Hyonic PE-90. Subsequent studies (Texas Research Institute, 1982) in large scale model aquifer systems have confirmed that surfactant solutions can enhance gasoline recovery, but that recovery efficiencies are influenced by the method of surfactant application.

Based on the results of the Texas Research Institute (1979, 1982) studies, a laboratory study of the solubilization of various common contaminants by water washes and by a surfactant mixture was conducted by Ellis et al. (1984). The contaminants tested included:

TABLE 3-3

SUMMARY OF EXPERIMENTS ON SURFACTANT-ENHANCED GASOLINE RECOVERY(1)

SURFACTANTS(2)	STRUCTURE	WATER SOLUBILITY	INTERFACIAL TENSION (Y) (dynes/cm)	ENHANCED GASOLINE RECOVERY
Deionized Water			11.5	
NONIONICS				
Hyonic PE-90 (DS)	Polethoxylate nonylphenol	Clear Solution	0.12	None Observed
Hyonic PE-190 (DS)	Polyethoxylate nonyl phenol	Clear Solution	0.72	(3)
Hyonic PE-120 (DS)	Polyethoxylate nonyl phenol	Clear Solution	1.2	-
Poly-Tergent B-500 (0)	Polyethoxylate nonyl phenol	Soluble	1.3	None Observed
Alrosol (0)	Oleic fatty acid amide	Dispersible	1.9	None Observed
ANIONIC				
Dupanol G (D)	Fatty alcohol amine sulfate	50%	1.0	-
Aerosol-OT (C)	Na dioctyl sulfosuccinate	15 g/1	1.2	-
Alfonic 1412-S (CO)	Linear $C_{12}-C_{14}$ H_{25-29} $(OCH_2CH_2)_3OSO_3-Na^+$			
Richonate YLA (R)	Dodecyl benzene sulfonate, isopropylamine salt	Soluble	2.4	None Observed
C-550 Slurry (CO)	Linear alkyl benzene sulfonate, Na salt	Soluble H_2O/ETHOH	0.61	Moderate
Aerosol-MA (C)	Na dihexyl sulfosuccinate	Soluble alcohol	1.2	-
Sarkosyl-NL (CG)	Lauroyl sarcosinate, Na salt	343 g/1 25°C	7.1	-
		Soluble as Na salt	1.8	-

TABLE 3-3 (Cont'd)

SURFACTANTS(2)	STRUCTURE	WATER SOLUBILITY	INTERFACIAL TENSION (Y)	ENHANCED GASOLINE RECOVERY (dynes/cm)
FLUOROCARBON				
Zonyl FSN 0.05% (D)	Fluorocarbon	Greater than 2%	3.9	-
Zonyl FSN 0.05% (D)	Fluorocarbon	Greater than 2%	11.0	-
Lodyne S-102 0.1%(CG)	Sodium fluorinated alkyl sulfonate	Soluble	2.3	-
Lodyne S-102 0.05%(CG)	Sodium fluorinated alkyl sulfonate	Soluble	3.2	-
Lodyne S-111 0.05%(CG)	Sodium fluorinated alkyl sulfonate	Soluble	6.9	-

Notes

(1) Adapted from American Petroleum Institute, (1979). Surfactant concentration 0.1% unless otherwise noted.

(2) Letters in parenthesis refer to manufacturers:

DS - Diamond Shamrock	C - Cyanamid
O - Olin	CO - Conoco
D - DuPont	CG - CIBA - GEIGY
	R - Richardson

(3) Dash (-) indicates not tested.

- intermediate and high molecular weight aliphatics and polynuclear aromatics (PAH) derived from crude oil,
- PCBs in chlorobenzenes (Askarel), and
- Di-, tri-, and pentachlorophenols.

The soil used was a fine-to-coarse loam (gravelly silty sand) with a permeability of 10^{-2} to 10^{-4} cm/sec (28 to 0.28 ft/day) but low organic carbon content (0.1%). A series of shaker table extractions and 1 meter (3 foot) long soil column extractions were performed. The former gave the maximum extraction efficiency under soil washing conditions with agitation, while the latter tests showed the potential extraction efficiencies under gravity flow without agitation. Initially, a mixture of 2% Richonate YLA and 2% Hyonic PE-90 was tested. However, this mixture tended to suspend (disaggregate) silt and clay grains, which clogged the soil columns. A mixture of 2% Hyonic PE-90 with 2% Adsee 799 (both nonionic surfactants) was subsequently used.

Table 3-4 gives the results of these studies. Water washes were ineffective in solublizing either the aliphatic/PAH or the PCB mixtures. However, after three pore volumes of the surfactant had passed through the soil columns, only 11% of the aliphatic/PAH mixture and 14% of the PCB mixture remained in the soils. After ten pore volumes of surfactant flushing 7 and 3 percent respectively of the aliphatic/PAH and PCB mixtures remained in the soil. Subsequent water rinses did not reduce these residual concentrations.

In contrast, the initial water washes removed over 99% of the phenol mixture (Table 3-4), with the surfactant washes removing much of the residual 1%. These results demonstrate the efficiency of surfactant solubilization of hydrophobic compounds such as aliphatics, PAH and PCB, and the fact that surfactant-assisted flushing is not necessary for hydrophilic compounds such as phenols.

TABLE 3-4

RESULTS OF SURFACTANT-FLUSHING OF CONTAMINANTS FROM TEST SOIL

Contaminant Mixture	Test Type	Percent of Contaminants Remaining in Soil														
		Water Washes					Surfactant Washes					Water Rinses				
		1	2	3	4-7	8-10	1	2	3	4-7	8-10	1	2	3	4-7	8-10
A	Shaker	96	93	91	-	-	42	26	27	-	-	25	10	10	-	-
A	Column	-	100[b]	-	100	100	-	11[b]	-	9	7	-	9[b]	-	7	7
B	Shaker	100	100	100	-	-	35	18	12	-	-	5	9	7	-	-
B	Column	-	100[b]	-	100	100	-	14[b]	-	3	3	-	3[b]	-	4	2
C	Column	-	3[b]	-	1	0.8	-	0.1[b]	-	0.1	0.1	-	0.1[b]	-	0.1	0.1

A = high MW aliphatics and polynuclear aromatics.

B = PCBs in chlorobenzenes

C = di-, tri-, and pentachlorophenols

a. number of pore volumes of eluant (water or surfactant solution)

b. pore values 1-3 combined for column tests

3.5 Surfactant Application to Subsurface Deposits: Geochemical and Environmental Factors

The application of surfactant solutions to organic waste deposits requires consideration of not only the chemical characteristics of the surfactant and the waste but also of the environmental and geochemical factors which may affect surfactant use. The latter can impose a variety of constraints on the potential effectiveness of surfactant applications by impairing surfactant delivery to the waste deposit, altering the chemical activity of the surfactant or generating an environmental chemical hazard resulting from the surfactant itself or a side reaction product. The principal geochemical constraints may arise through interactions between the surfactant and site soils or groundwater.

3.5.1 Groundwater Chemistry

The chemical composition of site groundwater can alter or inhibit the effectiveness of surfactants. Inhibition can result from a variety of reactions which either remove the surfactant from solution (precipitation) or reduce the effectiveness of the surfactant (neutralization, complexing). Among those groundwater chemical conditions which may influence surfactant effectivness are ionic strength, polyvalent ion concentrations, and pH levels. Many surfactants are optimally effective only within limited ranges of ionic strength and electrolyte composition. In particular, many surfactants lose their effectiveness or precipitate at high divalent ion (Ca and Mg) concentrations (i.e., in "hard" waters - this is why water softeners or ion exchange resins are used to pretreat such waters before addition of detergents in industrial and household applications).

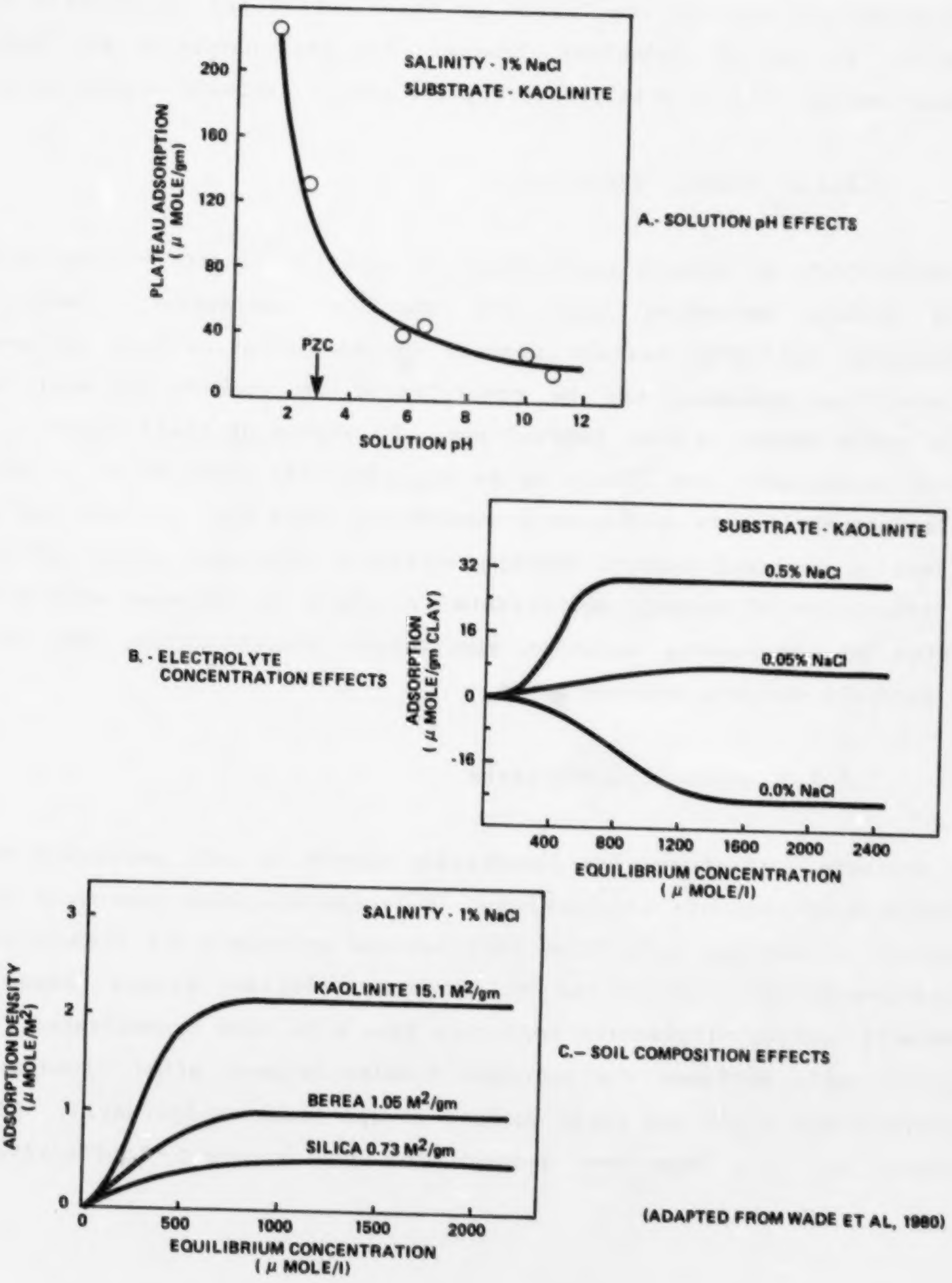
3.5.2 Soil Chemistry

Surfactant effectiveness may also be inhibited by chemical adsorption to soil particles, thereby reducing the aqueous surfactant concentration. The extent of adsorption of a given surfactant will be a function of several factors, including surfactant structure, soil composition, particle size and surface area, and groundwater chemical composition. In general, soils of small particle size and high surface area per unit weight (e.g., high clay content) are likely to provide conditions under which maximum surfactant adsorption may occur.

An example of the combined influence of soil and groundwater chemical interactions on surfactant adsorption to soils is depicted in Figure 3-1. Figure 3-1A shows that the adsorption of the anionic surfactant 4-phenyl dodecyl benzene sulfonate markedly increases as the aqueous solution pH is decreased below the point of zero charge (PZC) of the kaolinite substrate (approximately pH 5, below which the clay surface has a net positive charge and will adsorb the negatively charged surfactant hydrophilic groups). Kaolinite clay particles and most other silicate mineral surfaces possess PZCs in the acidic pH range, and are therefore negatively charged under most natural water pH conditions (Parks, 1967), where adsorption of anionic surfactants would not be a problem. Increasing electrolyte concentrations also tend to increase the amount of surfactant adsorption to the kaolinite substrate (Figure 3-1B), possibly through a neutralization of the negative charge on the clay particle surfaces. Figure 3-1C depicts the influence of substrate composition on surfactant adsorption. These results demonstrate that surfactant adsorption increases with increasing solid phase surface area, with the greatest adsorption being to kaolinite clay. Overall, these results suggest that for this surfactant, and probably other anionic surfactants, minimum soil adsorption losses would occur under conditions of alkaline solution pH, and at low electrolyte concentrations in soils of low particle surface area.

The principal implications of the preceeding and other available information concerning geochemical interactions likely to be observed in specific surfactant classes may be summarized as follows:

FIGURE 3-1
THE EFFECTS OF SOLUTION pH, ELECTROLYTE COMPOSITION AND SOIL COMPOSITION ON SURFACTANT ADSORPTION TO SOIL



A.- SOLUTION pH EFFECTS

B. - ELECTROLYTE CONCENTRATION EFFECTS

C.– SOIL COMPOSITION EFFECTS

(ADAPTED FROM WADE ET AL, 1980)

3.5.2.1 Cationic Surfactants

The surfaces of typical soil particles (such as clays) are negatively charged under typical soil pH conditions (pH 5-8). Therefore, most if not all cationic surfactants are likely to be readily adsorbed to soil particles under these conditions and are not likely to be effective for application to waste deposits. At low pH conditions, however, the soil particles may have a net positive charge (Figure 3-1A), favoring the use of cationic surfactants.

3.5.2.2 Anionic Surfactants

The sensitivity of anionic surfactants to solution electrolyte concentrations varies widely depending upon the specific surfactant. Many anionic surfactants, including certain members of the fluorocarbon, sulfonate and sulfosuccinate classes, may be precipitated in groundwater with hardness levels which exceed several hundred ppm. By virtue of their negative charge, anionic surfactants are likely to be significantly less prone to adsorption (and consequently more mobile in groundwaters) than are cationic surfactants. The data on 4-phenyl dodecyl benzene sulfonate discussed above indicate that soil adsorption of anionic surfactants is likely to increase with decreasing solution pH, increasing solution electrolyte concentration, and increasing soil particle specific surface areas.

3.5.2.3 Nonionic Surfactants

Many nonionic surfactants may potentially adsorb to soil particles through a combination of nonionic interactions. Polyoxyethylenated nonionics are known to adsorb to nonpolar substrates from aqueous solutions via dispersion forces or hydrophobic bonding off the hydrophobic surfactant groups (Rosen, 1978). Conversely, polyoxyethylenated nonionics have also been demonstrated to adsorb on polar solid surfaces via hydrogen bonding between ether linkages of the polyoxyethylene chain and polar surface groups (such as hydroxyl). Adsorption processes of this type may account for the apparent ineffectiveness of nonionic surfactants in enhancing gasoline recovery, despite the fact that these surfactants display excellent aqueous/gasoline interfacial tension reduction properties.

3.5.2.4 Amphoteric Surfactants

The presence of both positive and negative charge sites (the amphoteric characteristic) on these surfactants suggests that they are more likely to adsorb to soil particles than otherwise similarly structured anionic surfactants under similar solution chemical conditions. Based on their structural characteristics, amphoteric surfactants would be expected to undergo ionic adsorption to soil particles with maximum adsorption occuring under pH conditions wherein the surfactants display cationic charge properties.

3.5.2.5 Anionic - Nonionic Surfactant Mixtures

Limited available data (Wade et al., 1980) indicate that mixtures of anionic and nonionic surfactants demonstrate complex adsorption behavior with the extent of the adsorption to a soil dependent at least in part upon the mole ratios of the surfactants in the mixture. Of interest was the observation that at certain mole ratios, mixtures of an anionic surfactant (3-phenyl undecyl benzene sulfonate) and certain nonionic surfactants (ethoxylated nonylphenols) demonstrated less adsorption to a kaolinite substrate than did either of the surfactants tested individually. These results suggest that anionic/nonionic surfactant mixtures might be formulated to minimize geochemical interactions in applications to solid waste deposits.

3.6 Environmental Effects

The introduction of surfactant solutions into surface and groundwater systems requires consideration of possible adverse environmental effects. The surfactant characteristics of principal environmental concern are biodegradability, toxicity to plants and animals, and human health hazards both during and after application.

3.6.1 Biodegradability

The application to soils and groundwaters of any surfactant which is strongly resistant to biodegradation may result in the generation of new environmental chemical problems at a waste site beyond those which already exist. However, in the case of application to waste deposits, a converse problem also exists -- surfactants which are too rapidly biodegraded may not retain surface activity for time periods sufficient to complete the in situ treatment process. Available evidence indicates that most commercially available surfactants are biodegradable, although degradation rates of surfactants under the range of geochemical conditions of interest in waste treatment are lacking. Sivik et al. (1982) reviewed the biodegration of selected major surfactants including C_{12} homologs of the following classes:

- linear alkylbenzene sulfonates,
- alkyl sulfates,
- alpha olefin sulfonates,
- secondary alkane sulfonates,
- alcohol ethoxy sulfates,
- alkyl phenol ethoxylates, and
- alcohol ethoxylates.

Results of BOD, CO_2 evolution, and simulated treatment process tests indicated that for all of the tested compounds significant degradation (greater than 50%) was observed in less than 20 days. Die away tests suggested 90-100% decreases in surfactant concentrations in less than 10 days for the compounds tested (Sivik et al., 1982).

Available manufacturer's information included in Table 3-5 indicates generally rapid degradation of certain sulfosuccinates, sulfonates, and alkyl sulfates and somewhat slower rates for alcohol ethoxylates. Quantitative data for the fluorocarbons were unavailable but biodegradation is likely to be somewhat slower than for the other listed compounds. Data for nonionic surfactants indicate alkyl chains to be more rapidly degraded than ethylene oxide chains, and alkylphenol ethoxylates to be somewhat more slowly degraded.

TABLE 3-5

ENVIRONMENTAL CHEMICAL PROPERTIES OF SELECTED COMMERCIAL SURFACTANTS(1)

SURFACTANT CLASS	EXAMPLE	WATER SOLUBILITY	ELECTROLYTE TOLERANCE (HARDNESS - PPM)	PH OF AQUEOUS SOLUTIONS(1)	BIODEGRADATION	TOXIC LEVELS(2)
Fluorocarbons	o Lodyne Series (CIBA-GEIGY)	o Soluble	o 300	5.0 - 8.5 (1%)	o Slow?	o 3-10 gm/kg o Acute Dermal LD50 (Rabbit) 3-10gm/kg
	o Zonyl Series	o >2gms/100gms	-		o Slow?	o 1-25 gm/kg
Sulfonates (Anionics)	Alkanol Series (DuPont)	o Soluble	-	7.5 - 10.0 (1%)	o Biodegraded	
Alcohol Ethoxylates (Nonionic)	o Merpol Series (DuPont)	o Generally >30%	o Electrolyte Tolerant?	6.0-9.0 (1%)	o Biodegraded (20-60% in 20 days with acclimated bacteria)	o Acute Oral Toxicity for Fish 1-6 mg/L
Sulfosuccinates (Anionic)	OT & Aerosol Series (Cyanamid)	o 1-60gms/100ml	o 500-2500	5.0 - 8.0	o 50-100%- 8 days (CSMA-Shake Culture Test)	o 1-10 ml/kg
Alkyl Sulfates (Anionic)	Duponol Series (DuPont)	o Soluble	o Electrolyte Tolerant	7.5 - 11.0 (3%)	o Biodegraded (days to weeks)	o 2-20 gm/kg o Acute Oral Toxicity to Fish 5-20 mg/l

(1) Parenthesis indicate concentration of surfactant.

(2) Toxicity reported as acute oral for rats unless otherwise specified.

In general, within a given surfactant class, biodegradation rates were found (Sivik et al., 1982) to vary with:

- the length of alkyl chains,
- the positions of phenyl groups, and
- the extent of chain branching.

Under the anaerobic conditions which may exist in organic waste deposits and associated groundwaters, degradation rates are likely to be considerably slower than under aerobic conditions. Qualitative data suggest that at least certain types of surfactants (sulfates and sulfonates) will eventually degrade in anaerobic environments (Sivik et al, 1982).

3.6.2 Toxicity

A detailed evaluation of the toxicity of the many commercially available surfactants is beyond the scope of this study. For comparative purposes, manufacturer-supplied toxicity data are included in Table 3-5. Sivik et al. (1982) noted that commonly reported LC_{50} values (for 24-96 hour studies) ranged from 1-50 mg/l for fish and 1-300 mg/l for invertebrates for:

- linear alkylbenzene sulfonates,
- alkyl sulfates,
- alpha olefin sulfonates,
- secondary alkane sulfonates,
- alcohol ethoxy sulfates,
- alkylphenol ethoxylates, and
- alcohol ethoxylates.

In general, increases in carbon chain length up to C_{16} were observed to significantly increase toxicity, with toxicity decreases observed for longer chain lengths. Based on an evaluation of rat LD_{50} data for the health hazards to humans posed by surfactants, Sivik et al. (1982) indicated that surfactants in general possess a relatively low level of acute mammalian toxicity. Acute oral LD_{50} values for rats were generally found to range from 650 mg/kg to greater than 3000 mg/kg. Other data from the literature suggest no chronic effect levels in the range of 0.1% - 1.4% in diet or 0.01% in drinking water.

3.7 Summary

The results of this study suggest that while selective surfactant applications might be utilized to effectively enhance recoveries of organics in certain waste and soil conditions, a substantial amount of detailed laboratory and pilot scale research will be required for the specific waste/soil/groundwater conditions at each site. Specific qualitative conclusions of this study include the following:

- Surfactant application to waste deposits warrants serious consideration as a means of reducing aqueous/organic interfacial tensions, making the organics more accessible to other means of degradation, and possibly enhancing the ability of aqueous solutions to flush insoluble organics from subsurface soils.

- Although comprehensive interfacial tension data are lacking for most surfactant/water/organic systems, there appear to be a number of relatively inexpensive and environmentally safe, commercially available classes of surfactants which should significantly reduce interfacial tensions in many aqueous/organic systems of interest in waste treatment. Surfactant classes which may be particularly effective in this regard include anionic fluorocarbons, anionic sulfonates, and nonionic alcohol ethoxylates.

- Available information suggests that a single chemical chracteristic of a surfactant or surfactant/water/organic system (for instance interfacial tension) can not effectively predict the overall likelihood of surfactant effectiveness in waste treatment.

Experimental measurements of properties (particularly interfacial tension) for relevant organic systems can, however, provide a method of initially screening specific surfactants for potential inclusion in more detailed studies (i.e., batch or column soil studies).

- The feasibility of solubilizing organics in concentrated surfactant solutions warrants further consideration but may be somewhat constrained because of the high surfactant solution concentrations and volumes required to effect significant solubilization of large organic deposits, and difficulties in surfactant recovery for recycling.

- The use of surfactants to promote emulsification is likely to be constrained by the complexity of emulsification processes, including the possible need for mechanical energy to generate an emulsion, the potential for reversibility of oil emulsions in aqueous systems, and the potential for phase separation and organic readsorption to soils.

- The likelihood of chemical interactions with soil particles or groundwater constituents presents a potentially serious constraint to the use of any surfactant type in soil systems. Anionic and nonionic surfactants should be least affected by soil adsorption reactions at normal soil pH (when soil particle surfaces are negatively charged), while cationic surfactants would be adsorbed most strongly. With decreasing soil pH, the soil particles will eventually become positively charged (Figure 3-1A), at which point the anionic surfactants will be adsorbed most while cationic surfactants would be least adsorbed. Adsorption to soils and the resultant loss in effectiveness preclude the consideration of cationics for waste treatment. The "custom synthesis" of anionic-nonionic surfactant mixtures should be considered as a means of minimizing adsorption effects.

- Within given classes, surfactants possess sufficiently varied chemical characteristics with respect to aqueous solubility, electrolyte and solution pH tolerance such that these properties should not pose insurmountable limitations to application in most groundwaters of low to moderate hardness (1-500 ppm).

- Under aerobic conditions, most commercial surfactants are effectively biodegraded in relatively short time frames (days to weeks), and effectiveness for in situ treatment might actually be inhibited by overly rapid degradation rates. Under anaerobic conditions degradation rates may be much slower and of greater environmental concern in removing residual surfactants, particularly with respect to anionic fluorocarbons and nonionic ethoxylated phenolics, which may degrade very slowly.

In order to better define the likelihood of success of surfactant applications to organic waste deposits additional information is required. In view of the chemical complexity of organic waste mixtures and the apparent limitations of aqueous/organic interfacial tension measurements in predicting the effectiveness of surfactants, the emphasis of further research should be on laboratory scale studies, possibly including:

- initial screenings of the effectiveness of specific surfactants to reduce the interfacial tensions of various pure and mixed organic phases, followed by,

- tests of the efficiency and effectiveness of specific surfactants to remove organics in soil columns or similar simulation systems.

Emphasis of such studies should be placed on the investigation of mixed surfactant systems since it is less likely that single surfactant systems will possess the combination of surface active characteristics required for maximum surface activity while simultaneously possessing the optimal characteristics to minimize processes such as soil adsorption.

3.8 Conclusions

For waste deposits containing organic compounds of relatively high water solubility (greater than 5×10^{-2}M), flushing with aqueous solutions alone (without surfactant addition) may prove to be an effective treatment process and should be considered. For deposits containing significantly less soluble organic compounds which possess moderately high octanol-water partition coefficient values (log K_{ow} greater than 2) flushing with aqueous solutions alone may prove to be of limited effectiveness. For these deposits, the use of surfactant solutions may enhance recovery efficiencies. However, prior to the application of surfactant solutions to waste deposits, laboratory research must be conducted to determine both the most appropriate surfactant (or mixture) for a particular waste in terms of the desired surface chemical properties and also the most effective surfactant in terms of minimizing unwanted interactions with subsoils.

The limited data base on surfactant use in soil systems is largely confined to considerations of surfactant application to petroleum and petroleum derived compounds and mixtures, including various component aliphatic and aromatic hydrocarbons. Therefore, it is for these types of waste deposits that surfactant applications may hold the greatest near term potential. Application to other types of organic contaminants is possible but would require considerably more background research.

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SECTION 4
HYDROLYSIS

4.1 Introduction

Hydrolysis is a chemical reaction in which a compound reacts with water, leading to cleavage of a bond in the compound. A common form of hydrolysis can be expressed as a displacement reaction,

$$RX + H_2O = ROH + HX, \tag{4-1}$$

where R represents an organic moiety and X the cleaved group in the hydrolysis reaction. In aqueous systems under typical environmental conditions, hydrolysis represents a major degradation mechanism for many organic chemicals. However, data with which to evaluate the contribution of hydrolysis to degradation of chemicals in waste deposits is limited. Therefore this section will review the basic controlling mechanisms of hydrolysis in the environment, present methods of estimating hydrolysis rates in waste deposits, and evaluate means of accelerating hydrolysis rates as a potential treatment method for waste deposits.

The primary data sources for this section are recent reviews which cover hydrolysis under environmental conditions (Harris, 1982; Mabey and Mill, 1978; Mill 1979; Radding et al., 1977; Versar, Inc, 1979). These reviews include extensive compilations of hydrolysis data including, in many cases, hydrolysis rate constants, conditions, half-lives and other data for a wide variety of organic compounds. These compilations, however, are not complete, and considerable additional data on hydrolysis are available in the recent literature. A comprehensive compound-by-compound review of the literature is beyond the scope of this work. However, the reader should be aware that a compound-specific search of the literature may provide data on hydrolysis rates for numerous organic compounds not included in this report or the primary data sources listed above.

4.2 Hydrolysis Mechanisms and Kinetics

In general, hydrolysis proceeds by attack of a nucleophile (e.g., water or hydroxyl ion) on an electrophile (e.g., carbon or phosphorus), resulting in displacement of a cleaved group. The reaction rate may either be independent of nucleophile concentration (unimolecular reaction) or be a function of the nucleophile concentration (bimolecular reaction).

Hydrolysis may occur through a variety of reaction pathways. In some cases, various hydrolysis mechanisms may be competing in a molecule with multiple functional groups. For example, Harris (1982) reports studies of malathion hydrolysis in which both carboxylate ester cleavage and phosphorodithioate ester cleavage can be significant. While it is recognized that various hydrolysis pathways can result in different by-products, an attempt has not been made in this report to identify all of the potential products of hydrolysis for the compounds considered. Of course, this would be required for a specific application to ensure that the products do not present a greater contamination problem than the parent compound(s).

Hydrolysis rates discussed in this section are based upon the disappearance rate of the parent compound only, without respect to mechanism or by-product formation. The rate of hydrolysis reactions can be described by kinetic rate expressions. In almost all cases, hydrolysis appears to occur as a first-order or pseudo-first-order reaction in which the rate of disappearance of the substrate, RX, is proportional to the concentration of substrate:

$$-d(RX)/dt = k(RX) \tag{4-2}$$

The persistence, in terms of half-life, for a given substrate can be expressed as:

$$t_{1/2} = (\ln 2)/k = 0.693/k \tag{4-3}$$

As will be discussed in greater detail below, half-lives for hydrolysis of organic chemicals may range from seconds (or less) to millions of years

(Harris, 1982; Mabey and Mill, 1978). The overall hydrolysis rate for a compound may be comprised of several separate reaction rates, namely those appropriate for neutral hydrolysis (rate independent of pH), acid-catalyzed hydrolysis (rate proportional to hydrogen ion concentration), and base-catalyzed hydrolysis (rate proportional to hydroxyl ion concentration). This will be described further below.

4.2.1 Hydrolyzable Organic Groups

Harris (1982) has tabulated organic functional groups which are susceptible to hydrolysis, as well as those which are resistant to hydrolysis. Compounds resistant to hydrolysis include unsubstituted hydrocarbons (aliphatic and aromatic), halogenated aromatics, PCBs, phenols, aromatic amines, and many other classes (Table 4-1). Organic functional groups susceptible to hydrolysis include alkyl halides, carbamates, nitriles, phosphoric and phosphonic acid esters, and several other functional groups (Table 4-2). It should be noted that a given organic molecule may contain both hydrolyzable and non-hydrolyzable functional groups since it may contain more than one functional group.

The reviews of hydrolysis cited in this report have focused primarily on the overall hydrolysis rate under neutral conditions (pH 7) at or near 25°C (77°F), as an indicator of the persistence of various chemicals under typical environmental settings. This approach provides a reasonably conservative estimate of half-life via hydrolysis, although in some cases, the half-life at pH 7 may be orders of magnitude shorter than the half-life at the minimum hydrolysis rate. For example, Zepp et al. (1975) have shown that the minimum hydrolysis rate of 2,4-D occurs at pH 3 to 4, and the hydrolysis rate at pH 7 is approximately three orders of magnitude above the minimum value.

From the perspective of stabilizing waste deposits via hydrolysis of organic contaminants, the hydrolysis rate at typical environmental conditions (i.e., at pH 7) is of limited interest, since chemicals which hydrolyze rapidly under these conditions would not be persistent in waste deposits. Therefore, it is

TABLE 4-1

GROUPS OF ORGANIC COMPOUNDS THAT ARE GENERALLY RESISTANT TO HYDROLYSIS[a] (Harris, 1982)

Alkanes
Alkenes
Alkynes
Benzenes/biphenyls
Polycyclic aromatic hydrocarbons
Heterocyclic polycyclic aromatic hydrocarbons
Halogenated aromatics/PCBs
Dieldrin/aldrin and related halogenated hydrocarbon pesticides
Aromatic nitro compounds
Aromatic amines
Alcohols
Phenols
Glycols
Ethers
Aldehydes
Ketones
Carboxylic acids
Sulfonic acids

---

[a] Multifunctional organic compounds in these categories may be hydrolytically reactive if they contain a hydrolyzable functional group in addition the functionality listed above.

TABLE 4-2

GROUPS OF ORGANIC COMPOUNDS THAT ARE POTENTIALLY TREATABLE BY HYDROLYSIS (Harris, 1982)

Alkyl halides

Amides

Amines

Carbamates

Carboxylic acid esters

Nitriles

Phosphonic acid esters

Phosphoric acid esters

Sulfonic acid esters

Sulfuric acid esters

---

the purpose of this section to examine the factors which control the hydrolysis rate of chemicals in order to determine the feasibility of accelerating hydrolysis rates of persistent chemicals in waste deposits. Factors controlling hydrolysis rates include pH, ionic strength, temperature, solvent composition, and catalysts. These factors are discussed below.

4.2.2 Effect of pH on Hydrolysis Rates

The hydrolysis rate of a given compound may be the sum of the neutral, acid-catalyzed, and base-catalyzed processes. The respective rate expressions for these processes are as follows:

$$-d(RX)/dt = k_N(RX) \qquad \text{(neutral hydrolysis)} \qquad (4\text{-}4)$$

$$-d(RX)/dt = k_A(RX)(H^+) \qquad \text{(acid-catalyzed hydrolysis)} \qquad (4\text{-}5)$$

$$-d(RX)/dt = k_B(RX)(OH^-) \qquad \text{(base-catalyzed hydrolysis)} \qquad (4\text{-}6)$$

Where k_N, k_A, and k_B are the neutral, acid-catalyzed, and base-catalyzed rate constants, respectively. The overall rate of hydrolysis of a compound is given by the sum of the rates of the contributing reactions:

$$-d(RX)/dt = k_N(RX) + k_A(RX)(H^+) + k_B(RX)(OH^-) \qquad (4\text{-}7)$$

At a fixed pH, the sum of these reactions appears as a pseudo-first order reaction in RX, where

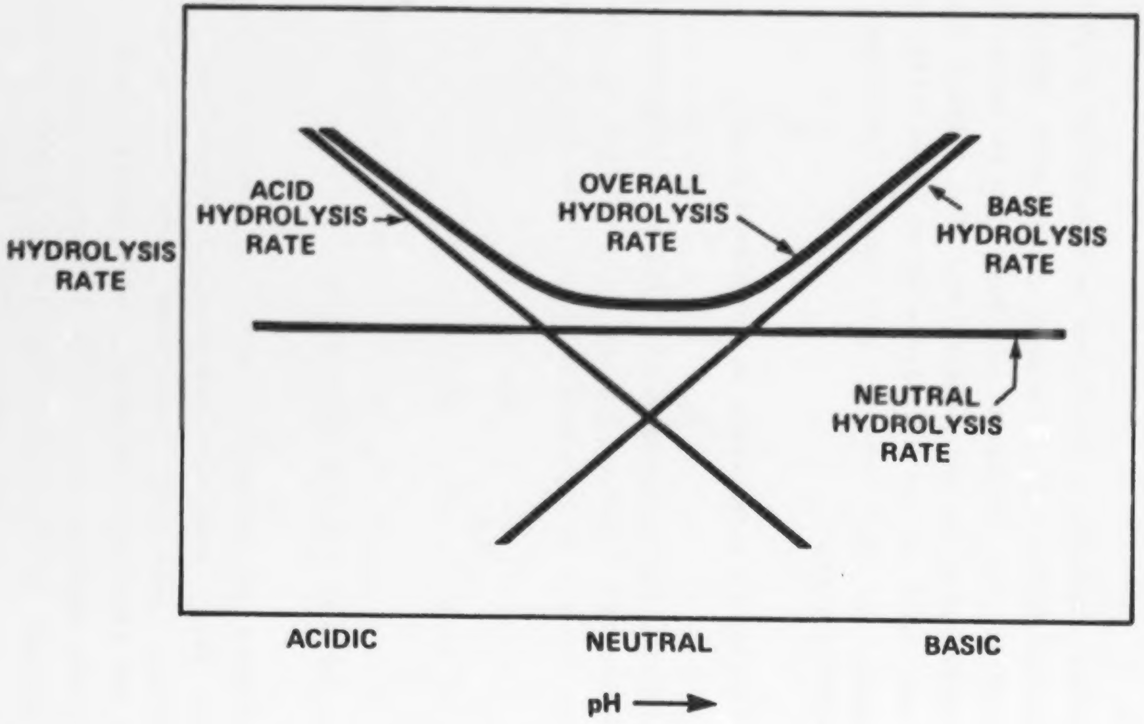
$$-d(RX)/dt = k_h(RX) \qquad (4\text{-}8)$$

The overall hydrolysis rate constant, k_h, is given by

$$k_h = k_N + k_A(H^+) + k_B(OH^-) \qquad (4\text{-}9)$$

Figure 4-1 illustrates the effect of pH on overall hydrolysis rate (Mabey and Mill, 1978). It is important to note that for substances where significant acid- or base-catalyzed reaction rates apply, the effect of a one-unit pH change is a one order of magnitude change in the overall hydrolysis rate.

FIGURE 4-1
pH DEPENDENCE OF HYDROLYSIS RATE BY
ACID, NEUTRAL, AND BASE PROMOTED PROCESSES



In order to discuss the effect of pH on half-lives for hydrolysis for specific compounds, kinetic data (rate constants) and other estimates of hydrolysis rates have been compiled from Mabey and Mill (1978), Harris (1982), Radding et al. (1977) and Versar Inc. (1979). These data are presented in Tables 4-3 through 4-10, and an example (hydrolysis of ethyl acetate) is illustrated in Figure 4-2.

Where possible, hydrolysis half-lives as a function of pH have been calculated from these available data. In many cases, data required to calculate the effect of pH are not available. It must also be noted that this compilation of hydrolysis rates is not exhaustive. The primary literature undoubtedly contains more data on the hydrolysis rates of specific chemicals of concern not included in this report, both under laboratory conditions and in environmental settings.

4.2.3 Effect of Temperature on Hydrolysis Rates

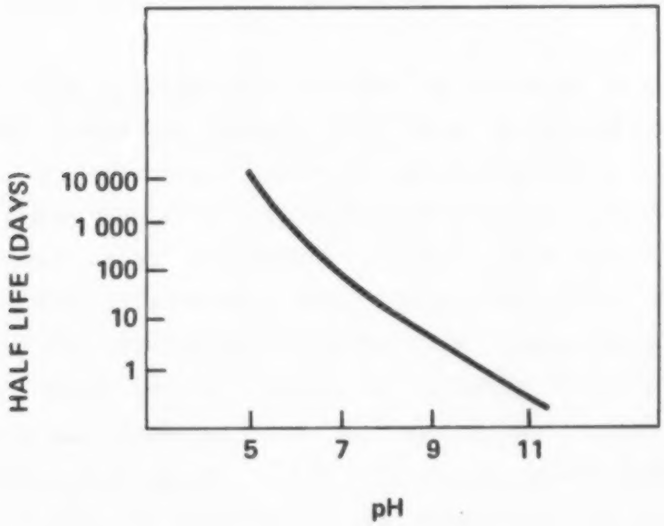
Several methods for estimating the effect of temperature on the hydrolysis rate constant are commonly applied in the study of kinetics (Zepp et al., 1975). One example is illustrated by reference to the Arrhenius relation:

$$k_h = Ae^{-E_A/RT} \tag{4-10}$$

where A is a constant, E_A is the Arrhenius activation energy, R the gas constant, and T is absolute temperature.

The dependence of hydrolysis rates on temperature must be considered in evaluating data, and may represent a significant source of error in extrapolating laboratory hydrolysis data to environmental conditions. Although the temperature dependence of hydrolysis rates is compound-specific, a generalized estimate that a 10°C decrease in temperature produces a factor of 2.5 decrease in hydrolysis rate is reasonable in the range of 0 to 50°C for most organic compounds (Mabey and Mill, 1978).

FIGURE 4-2
EFFECT OF pH ON HYDROLYSIS OF ETHYL ACETATE



Estimates of hydrolysis rates in the environment, including rates tabulated in this report, are usually based on for a temperature of 25°C. Waste deposit temperatures, in general, can be expected to be less than 25°C (unless containing an internal heat source, e.g., organic decomposition in a landfill). Typical non-thermal groundwater temperatures in the United States vary primarily with latitude, and generally range from about 5 to 27°C (40°F to 80°F) (Pettyjohn et al., 1979; Repa and Kufs, 1985). Seasonal temperature variations may be observed near the surface. If waste deposit temperatures are near ground water temperatures, hydrolysis rates in waste deposits in northern climates could be approximately a factor of 5 to 6 slower than those reported for 25°C (77°F).

4.2.4 Effect of Solvent Composition on Hydrolysis Rates

Hydrolysis rates are affected by solvent composition, with rates in water greater than rates for mixed water and organic solvents. For example, the hydrolysis rate of t-butylchloride increases approximately four orders of magnitude with a change in solvent composition from 90% ethanol/10% water to 100% water (Mabey and Mill, 1978). Hydrolysis rates reported for mixed solvents should be considered conservative estimates of hydrolysis rates for compounds dissolved in water. With water as the solvent for hydrolysis, rates may be affected by ionic strength (a measure of the total concentration of dissolved constituents), and increasing ionic strength can either accelerate or retard hydrolysis (Mabey and Mill, 1978). Total ionic strengths of less than 0.1 M (which is equivalent to a salinity of about 3000-6000 ppm, depending on the major ions present) are unlikely to have a significant affect on hydrolysis rates (less than 5 to 10%) according to Harris (1982).

4.2.5 Catalysis

Mabey and Mill (1978) report that alkaline earth and heavy metal ions can catalyze hydrolysis, apparently by increasing the effective OH^- ion concentration. If this postulate is correct, metal ion catalysis would appear to favor base-catalyzed hydrolysis processes. Specifically, copper, manganese, magnesium, and cobalt have been found to catalyze various reactions. However, Mabey and Mill (1978) indicate that metal ion catalysis is unlikely to affect hydrolysis rates at typical metal ion concentrations in the environment, although additional research would be necessary to determine the exact contributions of catalysis in specific environments. Harris (1982) reports that apparent hydrolysis rates in surface water in excess of predictions from laboratory results have been attributed to catalysis. At this time, the potential catalytic properties of metal ions, clay surfaces, etc., which may be present in a waste deposit cannot be predicted with any certainty.

Catalysis and retardation of hydrolysis rates of organic molecules by surfactants has also been reported (Fendler and Fendler, 1970; N L Wolfe, USEPA, Athens, GA, Personal Communication). However, simple rules for estimating this effect in environmental settings are not available.

4.3 Acceleration of Hydrolysis Rates in Waste Deposits

While a variety of factors may contribute to or affect the hydrolysis rate of organic chemicals in the environment, only the effects of pH and temperature can be characterized in a predictable manner. Temperature effects may be significant (e.g., a 25°C temperature increase may result in an order of magnitude increase in hydrolysis rates); however, it is unlikely that such temperature increases can be achieved in any field setting for extended periods of time without enormous energy expenditures. For this reason, the only apparent feasible method of increasing hydrolysis rates of chemicals in a waste deposit is by controlling the pH regime of the deposit. In particular, hydrolysis appears to be a potentially attractive in situ treatment method for a number of organic substances subject to base-catalyzed hydrolysis, for which the hydrolysis rates can be increased dramatically in the range of pH 7 to 11, as discussed below. Acid-catalyzed hydrolysis is less desirable, since acid conditions can mobilize significant concentrations of naturally-occurring or pollutant trace metals, creating other contamination problems.

The selection of pH 11 as an upper limit of the pH range for hydrolysis rate calculations in this report is somewhat arbitrary, since higher pH values could theoretically be achieved by addition of strong bases to waste deposits. However, the solubilities of major soil constituents (silica, alumina and aluminosilicates such as kaolinite) increase at high pH (above pH 9 to 10) and increase substantially above pH 11 (Stumm and Morgan, 1980). For this reason, a pH value near 11 [$(OH)^- = 1 \times 10^{-3}$ moles/liter] is probably a reasonable upper limit of pH achievable under field conditions. The value of increasing the pH in order to accelerate the hydrolysis rate must consider the ratio of k_b/k_n. With pH = 11 being the approximate upper limit of pH achievable (i.e., $OH = 10^{-3}$) k_b must be 10^3 times k_n for the base-catalyzed rate to equal the neutral rate at a pH of 11, 10^4 times k_n at a pH of 10, etc (see equations 4-4 through 4-6). If the base catalyzed contribution to the overall hydrolysis rate is less than that obtained at neutral conditions alone, raising the pH is probably not advisable.

Hydrolysis in the waste deposit can be assumed to be primarily an aqueous phase reaction. Degradation rates of a compound sorbed to solid phases or present in organic phases may be significantly different from the rate applicable to the aqueous phase. As such, hydrolysis rates reported in this section are probably most valid for relatively soluble species, and in waste deposits where sorption is limited. The potential effect of increasing hydrolysis rates through base catalysis for various chemical classes susceptible to hydrolysis is discussed below.

4.3.1 Alkyl Halides

Alkyl halides generally hydrolyze according to Equation 4-1:

$$RX + H_2O = ROH + HX \tag{4-11}$$

Hydrolysis rates for alkyl halides are influenced by both neutral hydrolysis and base-catalyzed processes. Table 4-3 presents the calculated hydrolysis half-lives for a number of alkyl halides in the pH range of 5 to 11, based on reported hydrolysis rate constants. With the exception of polyhalomethanes (e.g., $CHBr_2Cl$), base catalysis is not significant below pH values of 11 to 13 (i.e., k_b is less than 10^3 times k_n). Furthermore, hydrolysis half-lives for alkyl halides (with the exception of some methyl and benzyl

TABLE 4-3

HYDROLYSIS OF ALKYL HALIDES

Class/Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
Alkyl Halides											
Methyl Fluoride	1	-	7.44E-10	5.82E-7	30y	30y	30y	30y	30y	30y	15y
Methyl Chloride	1	-	2.37E-8	6.18E-6	0.93y	0.93y	0.93y	0.93y	0.93y	0.93y	0.93y
Methyl Bromide	1	-	4.09E-7	1.41E-4	20d	20d	20d	20d	20d	20d	20d
Methyl Iodide	1	-	7.28E-8	6.47E-5	110d	110d	110d	110d	110d	100d	55d
Methylene Chloride	1	-	3.2E-11	2.13E-8	704y	704y	704y	704y	704y	704y	350y
CH_2CHCH_2Cl	1	-	1.16E-7	6.24E-5	69d	69d	69d	69d	69d	69d	44.9d
$C_6H_5CH_2Cl$	1	-	1.28E-5	-	15h	15h	15h	15h	15h	15h	15h
$C_6H_5CHCl_2$	1	-	1.56E-3	-	0.1h	0.1h	0.1h	0.1h	0.1h	0.1h	0.1h
$C_6H_5CCl_3$	1	-	6.3E-2	-	19s	19s	19s	19s	19s	19s	19s
CH_2CHCH_2Br	1	-	1.67E-5	-	12h	12h	12h	12h	12h	12h	12h
CH_2CHCH_2I	1	-	4.01E-6	-	2.0d	2.0d	2.0d	2.0d	2.0d	2.0d	2.0d
$p\text{-}CH_3C_6H_4CH_2Cl$	1	-	4.5E-4	-	0.43h	0.43h	0.43h	0.43h	0.43h	0.43h	0.43h
$C_6H_5CH_2Br$	1	-	1.45E4	-	1.32h	1.32h	1.32h	1.32h	1.32h	1.32h	1.32h
$p\text{-}CH_3C_6H_4CH_2Br$	1	-	2.67E-3	-	4.3m	4.3m	4.3m	4.3m	4.3m	4.3m	4.3m
CH_2BrCl	1	-	-	-	-	-	44y	-	-	-	-
$CHCl_3$	1	-	-	6.9E-5	350,000y	35,000y	3500y	350y	35y	3.5y	0.35y
$CHBrCl_2$	1	-	-	1.6E-3	13,700y	1370y	137y	13.7y	1.37y	50d	5d
$CHBr_2Cl$	1	-	-	8.0E-4	27,400y	2740y	274y	27.4y	2.74y	100d	10d
CH_2Br_2	1	-	-	-	-	-	183y	-	-	-	-
$CHBr_3$	1	-	-	3.2E-4	6,600y	6860y	686y	68.6y	6.86y	250d	25d
$CHICl_2$	1	-	-	8.0E-4	27,500y	2750y	275y	27.5y	2.8y	0.28y	10d
$CHFICl$	1	-	-	2.2E-1	-	-	1.0y	36.5d	3.7d	0.37d	0.037d
CCl_4, 1ppm	1	-	-	second order	-	-	7000y	-	-	-	-
CCl_4, 1000 ppm	1	-	-	second order	-	-	7y	-	-	-	-
1,1,1-Trichloroethane	2	-	-			-	0.5y	-	-	-	-
Tetrachloroethene					-	-	0.7y	-	-	-	-
1,2-dichloroethane	3	-	-	-	-	-	50,000y	-	-	-	-
1,2-dibromoethane	3	-	-	-	-	-	5,000y	-	-	-	-
Ethylchloride	3	-	-	-	-	-	40d	-	-	-	-
1,1-dichloroethane	2	-	-	-							
Hexachlorocyclopentadiene)	2	-	-	-	14d	14d	14d	14d	14d	-	-

Note: All values reported for 25± 5°C. Rate constants in sec^{-1}.
s = second
m = minute
h = hour
d = day
y = year

Data Sources:
1. Mabey and Mill, 1978
2. Versar, Inc, 1979
3. Radding et al., 1977

halides) are generally in the range of years. As such, attempts to increase in situ hydrolysis rates of alkyl halides through control of pH are unlikely to be effective, for the range of reasonably achievable pH values.

4.3.2 Halogenated Ethers, Epoxides, and Alcohols

Hydrolysis rates of halogenated epoxides and ethers are generally high even at neutral pH, with half lives reported in the range of days or less (Table 4-4). As such, these substances are unlikely to persist in the environment. Acceleration of hydrolysis of these substances is unlikely to be necessary.

Hydrolysis rates were collected for only two halogenated alcohols, 2-chloroethanol and 1-chloro-2-propanol; their reported hydrolysis half-lives at pH 7 are 21 years and 2 years, respectively. Data on the effect of pH on hydrolysis rates for these substances were not obtained.

In summary, the available data do not indicate the potential for enhancement of hydrolysis rates by pH control for in situ treatment of halogenated ethers, epoxides or alcohols in waste deposits.

4.3.3 Epoxides

Epoxides are hydrolyzed by acid-catalyzed and neutral processes. Hydrolysis rates for epoxides are generally high, with half-lives in the range of 15 days at pH 7 (Table 4-5). While hydrolysis rates for epoxides can be increased at low pH, this process is unlikely to contribute significantly to the treatment of these substances in waste deposits because of their limited persistence at neutral pH values.

4.3.4 Esters (Carboxylic Acid Esters)

Esters hydrolyze to form carboxylic acids and alcohols according to the reaction:

$$R_1C(O)OR_2 + H_2O = R_1C(O)OH + R_2OH \qquad (4\text{-}12)$$

TABLE 4-4

HYDROLYSIS OF HALOGENATED ETHERS,
EPOXIDES, ALCOHOLS

Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
Chloromethylmethylether	1	-	-	-	-	-	0.007s	-	-	-	
bis(Chloromethyl)ether	1	-	-	-	-	-	38s	-	-	-	
2-(Chloroethanol	1	-	-	-	-	-	21y	-	-	-	-
1-Chloro-2-propanol	1	-	-	-	-	-	2 y	-	-	-	-
2-Chloroethylvinylether	2	-	-	-	-	-	0.48 y	-	-	-	-
3-Chloro-,1,2 epoxy, 2-methyl propane	3	1.84E-3	5E-7	-	16d	16d	16d	16d	16d	16d	16d
Alpha-epichlorohydrin	3	8.0E-4	9.8E-7	-	8.2d	8.2d	8.2d	8.2d	8.2d	8.2d	8.2d
Epibromohydrin	3	6.1E-4	5E-7	-	16d	16d	16d	16d	16d	16d	16d

Note: All values reported for 25°C. Rate constants in sec^{-1}.

s = second
d = day
y = year

Date Sources: 1. Radding et al., 1977
2. Versar, Inc, 1979
3. Mabey and Mill, 1978

TABLE 4-5

HYDROLYSIS OF EPOXIDES

Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
1,2-Epoxy ethane	1	1E-2	6.7E-7	-	12d	12d	12d	12d	12d	12d	11d
1,2 Epoxy propane	1	4.6E-2	5.5E-7	-	7d	14.6d	14.6d	14.6d	14.6d	14.6d	14.6d
1,2 Epoxy-2-methyl propane	1	7.3E0	1.1E-6	-	0.1d	.95d	4.4d	6.8d	7.2d	7.3d	7.3d
1,2 Epoxy-3-hydroxy propane	1	2.5E-3	2.84E-7		26d	28d	28d	28d	28d	28d	28d
1,2-Epoxy-2-methyl-3-hydroxy propane	1	1.1E-2	4E-7	-	13d	16d	16d	16d	16d	16d	16d
1,2-Epoxy-2-methyl-3-chloropropane	1	1.84E-3	5E-7	-	15d	16d	16d	16d	16d	16d	16d
Trans-2,3 epoxy butane	1	1.2E-1	5E-7	-	4.7d	13d	15.7d	16d	16d	16d	16d
Cis-2,3-epoxy butane	1	2.4E-1	5E-7	-	2.8d	11d	15.3d	16d	16d	16d	16d
1,2-epoxy-1-phenylethane	2	-	-	-	-	-	15d	-	-	-	-
trans-1,2-epoxy-1 phenylpropane	2	-	-	-	-	-	14d	-	-	-	-

Note: All values reported at 25°C. Rate constants in sec^{-1}.
d = day

Data Sources: 1. Mabey and Mill, 1978
2. Radding et al., 1977

Acid-catalyzed, neutral, and base-catalyzed processes may contribute to hydrolysis of esters. Base-catalyzed processes dominate hydrolysis for many esters above pH values in the range of 5 to 7. Half-lives for hydrolysis of numerous aliphatic and aromatic acid esters are tabulated as a function of pH in Table 4-6. Reported half-lives at pH 7 for esters cover a wide range (from less than one day to over one hundred years). For essentially all esters listed in Table 4-6, hydrolysis half-lives can be reduced to tens of days or less in the pH range of 8 to 10. For example, the hydrolysis half-life of t-butyl acetate is reduced from 140 years to 5.5 days by increasing pH from 7 to 10. Thus, the acceleration of hydrolysis rates in waste deposits through base-catalyzed hydrolysis represents a potentially feasible method for in situ treatment of carboxylic acid esters.

4.3.5 Amides

Amides hydrolyze by acid- and base-catalyzed processes, forming carboxylic acids and amines according to the reaction (Mabey and Mill, 1978):

$$RC(O)NR_1R_2 + H_2O = RC(O)OH + R_1R_2NH \qquad (4\text{-}13)$$

Table 4-7 lists hydrolysis half-lives as a function of pH for various amides. These half-lives are generally long (years to thousands of years) at pH 7, but can be reduced substantially by increasing the pH, with calculated half-lives in the order of years or less at pH 11. Base-catalyzed hydrolysis may therefore provide a feasible degradation mechanism for amides in waste deposits, especially for chlorinated amides.

4.3.6 Carbamates

Carbamates may degrade by acid-catalyzed, neutral, or base-catalyzed hydrolysis processes, although data in Mabey and Mill (1978) and Ryckman (1984) indicate that base-catalyzed processes predominate. Carbamates are hydrolyzed to alcohols, amines, and CO_2 according to the reaction:

$$ROC(O)NR_1R_2 + H_2O = ROH + HNR_1\ R_2 + CO_2 \qquad (4\text{-}14)$$

TABLE 4-6

HYDROLYSIS OF ESTERS

Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
Ethyl Acetate	1	1.1E-4	1.5E-10	1.1E-1	16y	16y	2.0y	0.2y	7.3d	0.73d	0.073d
Isopropyl Acetate	1	6.0E-5	-	2.6E-2	35y	68y	8.4y	308d	31d	3.1d	0.31d
Butyl Acetate	1	1.3E-4	-	1.5E-3	1.6y	78y	140y	1.5y	015y	5.5d	0.5d
Vinyl Acetate	1	1.4E-4	1.1E-7	1.0E1	73d	67d	7.3d	0.8d	1.9h	12m	1.2m
Allyl Acetate	1	-	-	7.3E-1	30y	3.0y	110d	11d	1.1d	2.6h	0.26h
Benzyl Acetate	1	1.1E-4	-	2.0E-1	17y	10.4y	1.1y	40d	4.0d	9.6h	1h
O-acetyl phenol	1	7.8E-5	6.6E-8	1.4E0	119d	100d	38d	5.5d	0.57d	1h	5m
2,4-dinitrophenyl acetate	1	-	1.1E-5	9.4E1	17h	16h	9.4h	1.8h	0.2h	1.2m	1+1m
ClCH$_2$C(O)^{O}CH$_3$	1	8.5E-5	2.1E-7	1.4E2	23d	5.0d	14h	1.4h	8.3m	50s	5s
Cl$_2$CHC(O)OCH$_3$	1	2.3E-4	1.5E-5	2.8E3	11h	4.5h	38m	4.1m	255	2.5s	0.2s
Cl$_2$CHC(O)OC$_6$H$_5$	1	-	1.8E-3	1.3E4	6.4m	6.1m	3.7m	47s	4.7s	0.5s	0.05s
F$_2$CHC(O)OC$_2$H$_5$	1	-	5.7E-5	4.5E3	3.3h	1.9h	23m	2.6m	16s	1.6s	0.2s
Cl$_3$CC(O)OCH$_3$	1	-	7.7E-4	-	15m	15m	15m	15m	15m	15m	15m
F$_3$CC(O)OC$_2$H$_5$	1	-	3.2E-3	-	3.6m	3.6m	3.6m	3.6m	3.6m	3.6m	3.6m
F$_3$CC(O)OC(CH$_3$)$_3$	1	-	1.3E-3	-	8.9m	8.9m	8.9m	8.9m	8.9m	8.9m	8.9m
CH$_3$SCH$_2$C(O)OC$_2$H$_5$	1	-	-	9.2E-1	24y	2.4y	87d	8.7d	0.87d	2.1h	13m
CH$_3$S(O)CHC(O)C$_2$H$_5$	1	-	-	1.3E1	1.7y	62d	6.2d	0.62d	1.5h	9m	1m
(CH$_3$)$_2$SCH$_2$C(O)-OC$_2$H$_5$	1	-	-	2.0E2	40d	96h	9.6h	57m	5.7m	35s	3.5s
C$_2$H$_5$C(O)OC$_2$H$_5$	1	3.3E-5	-	8.7E-2	52.3y	24.4y	2.5y	91d	9.1d	0.9d	2.2h
C$_3$H$_7$C(O)OC$_2$H$_5$	1	1.8E-5	-	3.8E-2	100y	55y	5.8y	212d	21d	2.1d	5h
(CH$_3$)$_2$CHC(O)OC$_2$H$_5$	1	-	-	2.3E-2	960y	96y	9.6y	350d	35d	3.5d	0.35d
CH$_2$CHC(O)OC$_2$H$_5$	1	1.2E-6	-	7.8E-2	244y	35y	3.5y	128d	13d	1.3d	0.13d
trans-CH$_3$CHCHC(O)-OC$_2$H$_5$	1	6.3E-7	-	1.3E-2	1140y	160y	17y	1.7y	62d	6.2d	0.62d
CHCC(O)OC$_2$H$_5$	1	-	-	4.68E0	4.7y	170d	17d	1.7d	0.17d	24m	2.4m
C$_6$H$_5$C(O)OCH$_3$	1	4.0E-7	-	1.9E-3	3720y	1160y	118y	11.8y	1.2y	0.12y	4.4d
C$_6$H$_5$C(O)OC$_2$H$_5$	1	-	-	3.0E-2	730y	73y	7.3y	0.73y	27d	2.7d	0.27d
C$_6$H$_5$C(O)OCH(CH$_3$)$_2$	1	-	-	6.2E-3	3500y	350y	35y	3.5y	128d	12.8d	1.3d
C$_6$H$_5$C(O)OCH$_2$C$_6$H$_5$	1	-	-	8.0E-3	2700y	270y	27y	2.7y	99d	9.9d	1.0d
p-NO$_2$-C$_6$H4C(O)OCH$_3$	1	4.3E-7	-	7.4E-2	282y	30y	3.0y	0.3y	11d	1.1d	2.6h
p-NO$_2$-C$_6$H4C(O)OCH$_3$	1			6.4E-1	34y	3.4y	0.34y	12.4d	1.2d	2.6h	0.26h
p-NO$_2$-C$_6$H4C(O)-OC$_2$H$_5$	1	1.4E-7	-	2.4E-01	92y	9.2y	0.92y	34d	3.4d	0.34d	0.8h
1-C$_5$H4NC(O)OC$_2$H$_5$	1	-	-	5.4E-1	41y	4.1y	0.41y	15d	1.5d	3.6h	0.36h
o-C$_6$H$_4$[C(O;OC$_2$H$_5$]2	1	-	-	1.0E-2	2200y	220y	22y	2.2y	80.3d	8.0d	0.8d
o-C$_6$H$_4$[C(O)OCH$_2$-C$_6$H$_5$]2	1	-	-	1.7E-2	1300y	130y	13y	1.3y	47.5d	4.8d	0.48d
p-C$_6$H4(CCO)OCH$_3$]$_2$	1	-	-	2.5E-1	880y	88y	0.88y	32d	3.2d	7.7h	0.77h
p-C$_6$H$_4$[C(O)OC$_2$H$_5$]2	1	-	-	6.9E-2	320y	32y	3.2y	117d	11.7d	1.2d	2.6h

Note: All values reported for 25°C. Rate constants in sec^{-1}.

s = second
m = minute
h = hour
d = day
y = year

Data Source: 1. Mabey and Mill, 1978

TABLE 4-7

HYDROLYSIS OF AMIDES

Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
Acetamide	1	8.36E-6	-	4.71E-5	262y	2490y	3950y	465y	46.5y	4.65y	0.47y
Valeramide	1	5.43E-6	-	1.41E-5	404y	3950y	11,300y	1560y	156y	15.6y	1.0y
Isobutyamide	1	4.63E-6	-	2.40E-5	470y	4500y	7700y	915y	91.5y	9.2y	0.92y
Cyclopentanecarboxamide	1	2.34E-5	-	1.67E-5	93.9y	931y	5500y	1300y	1.32y	13.2y	132y
Methoxy acetamide	1	7.84E-6	-	3.95E-4	280y	1860y	500y	55.6y	5.6y	0.56y	20d
Chloroacetamide	1	1.1E-5	-	1.5E-1	84.5y	14.6y	1.46y	0.15y	5.5d	0.55d	1.3h
Dichloroacetamide	1	-	-	3.0E-1	73y	7.3y	0.73y	26.6d	2.7d	6.5h	0.6h
Trichloroacetamide	1	-	-	9.4E-1	23y	2.3y	0.23y	8.4d	0.84d	2.0h	12m
Bromoacetamide	1	-	-	1.03E-5	$2x10^6$y	$2x10^5$y	21,200y	2120y	212y	21.2y	2.1y
N-methylacetamide	1	3.2E-7	-	5.46E-6	6900y	58,600y	38,000h	4020y	402y	40y	4.0y
N-ethylacetamide	1	9.36E-8	-	3.10E-6	23,000y	$1.8x10^5$y	70,000y	7090y	709y	71y	7.1y

Note: All values at 25°C. Rate constants in sec^{-1}.
m = minute
h = hour
d = day
y = year

Data Source: 1. Mabey and Mill, 1978

Table 4-8 lists calculated hydrolysis half-lives as a function of pH for a number of carbamates. Hydrolysis half-lives for carbamates at pH 7 range from minutes to thousands of years. Calculations indicate that half-lives can be reduced to the order of years or less for most carbamates when pH is increased to the range of 10 to 11. The data in Table 4-8 indicate that base-catalyzed hydrolysis can contribute significantly to the degradation of a wide variety of carbamates in waste deposits through control of pH (see also Section 4.4 and Ryckman, 1984).

4.3.7 Phosphoric and Phosphonic Acid Esters

Phosphoric and phosphonic acid esters are hydrolyzed primarily by base catalyzed processes, resulting in P-O bond cleavage as illustrated in the reaction (Mabey and Mill, 1978):

$$ROPR_1R_2 + H_2O = HOPR_1R_2 + ROH \qquad (4\text{-}15)$$

Cleavage of C-O bonds in these esters may also occur through acid catalyzed or neutral processes (Mabey and Mill, 1978). Table 4-9 presents a compilation of hydrolysis half-lives as a function of pH for a variety of phosphonic and phosphoric acid esters, many of which are of environmental significance as pesticides and chemical warfare agents.

Half-lives for hydrolysis at pH 7 are generally in the range of years to thousands of years for many of these compounds, although half-lives on the order of days apply to several. Since base-catalyzed hydrolysis is the dominant mechanism for almost all of these compounds in the pH range of 5 to 11, increasing pH in a waste deposit can be expected to have a marked effect on their degradation. With few exceptions, pH values in the range of 9 to 11 result in calculated hydrolysis half-lives of one year or less for phosphoric and phosphonic acid esters. For this reason, control of pH in a waste deposit appears to be a feasible method of in situ treatment for these compounds.

TABLE 4-8

HYDROLYSIS OF CARBAMATES

Compound	Date Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
$CH_3OC(O)N(H)C_6H_5$	1	-	-	5.5E-5	$4x10^5y$	40,000y	4,000y	400y	40y	4y	146d
$C_2H_5O(CO)N(CH_3)C_6H_5$	1	-	-	5.0E-6	$4.4x10^6yr$	$4.4x10^5y$	44,000y	4,400y	440yr	44y	4.4y
$C_6H_5O(CO)N(H)C_6H_5$	1	-	-	5.42E1	150d	15d	1.5d	3.6h	21m	2m	13sec
$C_6H_5OCCO)N(CH_3)C_6H_5$	1	-	-	4.2E-5	$5.2x10^5y$	52,000y	5200y	520y	52y	5.2y	191d
$p-CH_3OC_6H_4(O)N(H)-C_6H_5$	1	-	-	2.5E1	320d	32d	3.2d	7.7h	46m	4.6m	28sec
$m-ClC_6H_4OC(O)N(H)-C_6H_5$	1	-	-	1.8E3	4.5d	11h	1.1h	6.4m	39sec	3.9sec	0.4sec
$p-NO_2C_6H_4OC(O)N(H)-C_6H_5$	1	-	-	2.7E5	43m	4.3m	26sec	2.6sec	0.3sec	0.03sec	0.003sec
$p-NO_2C_6H_4OC(O)N-(CH_3 \cdot C_6H_5$	1	-	-	8.0E-4	27,500y	2750y	275y	27.5y	2.7y	100d	10d
$1-C_{10}H9OC(O)N(H)CH_3$	1	-	-	9.4E0	2.3y	85d	8.5d	20h	2h	1.2m	74sec
$1-C_{10}H9OC(O)N(CH_3)_2$	1	-	1.8E-11	-	1200y	1200y	1200y	1200y	1200y	1200y	1200y
$(C_2H5)_2NCH_2CH_2OC-(O)N(H)C_6H_5$	1	-	-	2.6E-5	$8.5x10^5y$	85,000y	8400y	850y	85y	8.5y	310d
$(C_2H5)_2NCH_2CH_2OC-(O)N(H)C_6H_3(CH_3)_3$	1	-	-	9.4E-7	$2.3x10^7y$	$2.3x10^6y$	$2.4x10^5y$	23,000y	2300y	230y	23y
$(CH_3)_3NC_6H4OC(O)N-(H)CH_3$	1	-	-	6.7E-1	33y	3.3y	120d	12d	1.2d	2.9h	1.7m
$(CH_3)_3NC_6H4OC(O)N-(CH_3)_2$	1	-	-	2.8E-4	89,500y	7850y	785y	78.5y	7.9y	268d	29d
$ClCH_2CH_2OC(O)N(H)-C_6H_5$	1	-	-	1.6E-3	14,000y	1400y	140y	14y	1.4y	50d	5d
$Cl_2CHCH_2OC(O)NHC_6H_5$	1	-	-	5.0E-2	440y	44y	4.4y	160d	16d	1.6d	3.9h
$CCl_3CH_2OC(O)NHC_6H_5$	1	-	-	3.2E-1	69y	6.9y	252d	25d	2.5d	6h	36m
$CF_3CH_2OC(O)NHC_6H_5$	1	-	-	1.0E-1	220y	22y	2.2y	80d	8d	20h	2h
Ethyl carbamate	2	-	-	-	-	-	11,000y	-	-	-	-
$C_2H_5OC(O)NHCH_3$	2	-	-	-	-	-	38,000y	-	-	-	-
$C_2H_5OC(O)N(CH_3)_2$	2	-	-	-	-	-	39,000y	-	-	-	-

Note: All values at 25° C. Rate constants in sec^{-1}.
m = minute
h = hour
d = day
y = year

Data Sources: 1. Mabey and Mill, 1978
2. Radding et al., 1977

TABLE 4-9

HYDROLYSIS OF PHOSPHORIC AND PHOSPHONIC ACID ESTERS

Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
$CH_3P(O)(OCH_3)_2$	1	1.36E-9	-	2.5E-3	8700y	880y	88y	8.8y	321d	32d	3.2d
$CH_3P(O)(OC_2H_5)_2$	1	1.7E-9	-	2.2E-4	93,000y	9980y	990y	100y	10y	1y	36d
$CH_3P(O)(OCH(CH_3)_2)_2$	1	6.4E-9	-	3.2E-7	$3.4x10^5y$	$2.3x10^6y$	$6.6x10^5y$	69,000y	6900y	690y	69y
$CH_3P(O)(OC_2H_5)(O$-p-$C_6H_4NO_2)$	1	1.2E-7	-	4.0E-2	530y	55y	5.5y	200d	20d	2d	4.8h
$C_2H_5P(O)(OCH(CH_3)_2)_2$	1	3.2E-9	-	3.7E-8	$6.9x10^5y$	$6.2x10^6y$	$5.5x10^6y$	$5.9x10^5y$	59,000y	5900y	590y
$C_6H_5P(O)(OC_2H_5)_2$	1	1.1E-9	-	5E-4	43,000y	4400y	440y	44y	4.4y	160d	16d
$(CH_3O)_3PO$	1	-	1.8E-8	1.3E-4	1.2y	1.2y	1.22y	1.2y	1.1y	260d	54d
$(C_2H_5O)_3PO$	1	-	4E-9	8.2E-6	5.5y	5.5y	5.5y	5.5y	5.4y	4.6y	1.8y
$(C_2H_5S)_3PO$	1	-	1.4E-9	1.2E-2	16y	14y	8.5y	1.6y	66d	7d	16h
$(C_6H_5O)_3PO$	1	-	2.7E-11	1.7E-2	550y	112y	13y	1.3y	47d	5d	11h
$(C_2H_5O)P(O)($-p-$C_6H_4NO_2)$	1	-	3.3E-6	5.3E-1	2d	2d	2days	2d	9h	3h	22m
(p-$C_6H_4NO_2)_3PO$	1	-	1.0E-3	3.43E-1	12m	12m	11m	11m	9m	3m	20sec
$(CH_3O)_2P(S)$p-$C_6H_4NO_2$	1	-	1.1E-7	5.95E-3	73d	73d	72d	69d	47d	11d	1.3d
$CH_3OP(S)SCHCH$-$(CO_2C_2H_5)_2$	1	-	-	4.3E-0	5y	187d	18d	1.9d	4.5h	27m	3m
$(C_2H_5O)_2P(S)($p-$C_6H_4NO_2)$	1	-	3E-9	2.2E-4	7y	7y	7yr	7yr	4yr	321d	36d

Note: All values reported for T=25°C. Rate constants in sec^{-1}.
m = minute
h = hour
d = day
y = year

Data Source: 1. Mabey and Mill, 1978

4.3.8 Alkylating Agents, Pesticides and other Compounds

A number of compounds of potential environmental concern, including numerous pesticides, do not fit conveniently into a single chemical class. However, hydrolysis rate constants are available for some of these substances, and are compiled in Table 4-10. While generalities cannot drawn with respect to structure-reactivity relationships, it is apparent that base-catalyzed hydrolysis can contribute significantly to the degradation of numerous pesticides in the pH range of 5 to 11, which can have hydrolysis half-lives on the order of one year or less at pH 11 or less (Table 4-10). As such, control of pH in a waste deposit may be capable of increasing the degradation rate of these substances. Additional data upon which to evaluate the potential hydrolysis rates of other pesticides may be available in the primary literature, by search on a compound-specific basis.

4.4 Case History of Base-Catalyzed Hydrolysis

A warehouse fire at an agricultural warehouse in Hillsboro, IL led to contamination of soil and surface waters by a combination of 21 different pesticides, including carbamates, anilines, pyridines, organophosphates and benzoic acids (Ryckman, 1984). Bench scale studies were performed to evaluate potential treatment technologies, which included aeration, evaporation, alkaline hydrolysis, solar oxidation/photolysis, carbon adsorption and oxidation with hydrogen peroxide (Ryckman, 1984).

The contaminated surface waters were treated by aeration, solar oxidation, evaporation and powdered activated carbon adsorption/clarification. Forty thousand cubic feet of soils contaminated up to depths of 3 feet were detoxified in situ. Soda ash and powdered activated carbon were disced and plowed into the soil. Periodic application of soda ash maintained a pH of 9, and a water mist served to activate the ash. Some of the pesticides were degraded by soda ash alkaline hydrolysis. The activated carbon mitigated odors and absorbed agricultural chemicals to prevent further migration. In addition, the black carbon absorbed solar radiation, thereby elevating soil

TABLE 4-10

HYDROLYSIS OF MISCELLANEOUS COMPOUNDS (INCLUDING PESTICIDES)

Compound	Data Source	k_A	k_N	k_B	t 1/2 at pH						
					5	6	7	8	9	10	11
beta-Propiolactone	1	-	3.3E-3	-	3.5m	3.5m	3.5m	3.5m	3.5m	3.5m	3.5m
$CH_2CH_2S(O_2)$	1	-	2.15E-5	-	8.9h	8.9h	8.9h	8.9h	8.9h	8.9h	8.9h
Dimethyl sulfate	1	-	1.66E-4	1.48E-2	1.2h	1.2h	1.2h	1.2h	1.2h	1.1h	1.1h
Bis(chloromethyl) ether	1	-	2.8E-2	-	25sec	25sec	25sec	25sec	25sec	25sec	25sec
Phenyldimethyltriazine	1	-	2.75E-5	-	7h	7h	7h	7h	7h	7h	7h
Benzoyl chloride	1	-	4.2E-2	-	16sec	16sec	16sec	16sec	16sec	16sec	16sec
$(CH_3)_2NCO$	1	-	2.5E-3	-	4m	4m	4m	4m	4m	4m	4m
$CH_3OC(O)$	1	-	5.64E-4	-	20m	20m	20m	20m	20m	20m	20m
Methoxychlor	1	-	2.99E-8	3.64E-4	270d	270d	270d	267d	241d	121d	20d
Captan	1	-	1.87E-5	5.7E2	10h	8h	3h	20m	2m	12sec	1sec
Atrazine	1	3.9E-5	7.6E-5	-	2.5h	2.5h	2.5h	2.5h	2.5h	2.5h	2.5h
Malathion	2	4.8E-5	7.7E-9	5.5E0	1.6h	128d	14d	1.5d	3.5h	21m	2m
Parathion	2	-	4.5E-8	2.3E-2	178d	177d	170d	118d	29d	3.4d	8.4h
Paraoxon	2	-	4.1E-8	1.3E-1	195d	190d	149d	47d	6d	15h	1.5h
Diazinon	2	2.1E-2	4.3E-8	5.3E-3	32d	125d	176d	165d	14d	14d	1.5d
Diazoxon	2	6.4E-1	2.8E-7	7.6E-6	1.2d	9d	23d	28d	29d	29d	29d
Chlopyrifos	2	-	1.E-7	1E-1	80d	79d	73d	40d	7d	19h	2h
Sevin	2	-	-	7.7E0	2.9h	104d	10d	1d	2.5h	15m	1.5m
Sevin	2	-	-	3.4E0	6.5y	236d	24d	2.4d	5.7h	34m	3.4m
Baygon	2	-	-	4.6E-1	48y	4.8y	174d	17d	1.7d	4.2h	25m
Pyrolam	2	-	-	1.1E-2	2000y	200y	20y	2y	73d	7.3d	18h
Dimetilan	2	-	-	5.7E-5	$3.9x10^5$y	39,000y	3900y	390y	39y	3.9y	141d
P-Nitrophenyl-N-methyl carbamate	2	-	4E-5	3.0E3	4.5h	2.8h	34m	3.8m	23sec	2.3sec	0.23sec
2,4-D,m-butoxyethylester	2	2.0E-5	2.0E-5	3.02E1	9.6h	9.5h	8.4h	4.4h	36m	4m	23sec
Methoxychlor	2	-	2.8E-8	2.8E-4	286d	286d	286d	283d	252d	122d	20d
DDT	2	-	1.9E-9	9.9E-3	12y	11y	7.6y	1.9y	79d	8d	19h
2,4-D,methylester	2	-	-	1.7E1	1.3yr	47d	4.7d	11hr	1.1hr	6.8min	41sec

Note: All values for 25±5°C. Rate constants in sec^{-1}.
m = minute
h = hour
d = day
y = year

Data Sources: 1. Mabey and Mill, 1978
2. Harris, 1982

temperatures and catalyzing pesticide destruction (Ryckman, 1984). Periodic discing and soil aeration accelerated pesticide degradation by solar oxidation and volatile evaporation.

4.5 Summary

The discussion above indicates the potential application of base-catalyzed hydrolysis to accelerate degradation of a variety of organic compounds in waste deposits. However, it must be recognized that this discussion is based almost exclusively on data obtained in laboratory studies in controlled systems. At the present time, only limited investigations of hydrolysis rates in soil or sediment systems have been conducted (Wolfe, 1983), and there is very little practical field experience for control of hydrolysis rates in waste deposits. The data reported in this section should thus be used as a guide in selection of field situations where control of hydrolysis may provide a viable treatment alternative. Laboratory bench scale treatability studies and field pilot tests using site specific soil and waste matrices should be conducted prior to actual field implementation (e.g., Ryckman, 1984).

Although only one field experience with base-catalyzed hydrolysis has been reported in the literature (Ryckman, 1984), it is likely that conditions favorable to hydrolysis can be readily produced in many situations using available equipment, since the primary reagent is water, which can be introduced to a waste deposit using methods described in Chapter I (Delivery Systems). The alkaline conditions required to accelerate hydrolysis rates could be produced by addition of lime or soda ash to the soil surface followed by surface application of water (e.g., spraying or ponding). For deeper deposits, subsurface application of alkaline solutions could be utilized.

It is difficult, considering the scarcity of currently available data, to assess the potential interference of soil or waste deposit matrices on the hydrolysis process. Studies on a limited number of compounds in sediment-water systems conducted by Wolfe (1983) indicate that base-catalyzed processes are retarded for sorbed organic compounds, while neutral hydrolysis is unaffected. Hydrolysis rates of compounds in the aqueous phase of sediment-water systems are unaffected. Where much of the waste material is sorbed to solid phases, base-catalyzed hydrolysis rates may be limited kinetically by desorption rates which may be slow, since effective hydrolysis may occur primarily in the aqueous phase. Retardation of hydrolysis through sorption to solid phases can be expected to be greatest for compounds with a high octanol-water partition coefficient (this parameter represents a useful indicator for potential distribution of a compound between the aqueous and soil phases, see Section 3.3). Sorption of organic compounds in general is expected to be greatest for soils or deposits with high clay and organic content, and lowest for sands and gravels. However, the effect of sorption on hydrolysis can probably be determined quantitatively only through site-specific testing of a given waste material and solid matrix system.

Hydrolysis appears to present a relatively economical option for long term treatment of waste deposits since infrequent applications of chemicals (e.g., water and bases) can be expected to produce relatively long term modification of deposit conditions to favor degradation of those chemicals amenable to alkaline hydrolysis. However, dilution by groundwater flow, adsorption of atmospheric carbon dioxide, and other sources of acidity to the deposit are likely to require periodic addition of bases to maintain the desired pH in the deposit for long term treatment.

Based upon the data and calculations discussed in this chapter, the following classes of compounds are considered candidates for additional testing of the feasibility of base-catalyzed hydrolysis as an in situ degradation method:

- Esters,
- Amides,
- Carbamates,
- Phosphoric and Phosphoric Acid Esters, and
- Certain Alkylating Agents and Pesticides.

Potential application of base-catalyzed hydrolysis for various classes of compounds is summarized in Table 4-11.

TABLE 4-11

APPLICABILITY OF BASE CATALYZED HYDROLYSIS AS A TREATMENT METHOD FOR ORGANIC COMPOUNDS

Class of Compounds	Application of Base-Catalyzed Hydrolysis Indicated
Aliphatic Hydrocarbons	-
Alkyl Halides	(1)
Ethers	-
Halogenated Ethers and Epoxides	(2)
Alcohols	-
Glycols, Epoxides	(3)
Aldehydes, Ketones	-
Carboxylic Acids	-
Amides	+
Esters	+
Nitriles	(4)
Amines	(4)
Azo Compounds, Hydrazine Derivatives	-
Nitrosamines	-
Thiols	-
Sulfides, Disulfides	-
Sulfonic Acids, Sulfoxides	(5)
Benzene and Substituted Benzenes	-
Halogenated Aromatic Compounds	-
Aromatic Nitro Compounds	-
Phenols	-
Phosphoric and Phosphoric Acid Esters	+
Halogenated Phenolic Compounds	-
Nitrophenolic Compounds	-
Fused Polycyclic Hydrocarbons (PNAs)	-
Fused Non-Aromatic Polycyclic Hydrocarbons	-
Heterocyclic Nitrogen Compounds	-
Heterocyclic Oxygen Compounds	-
Heterocyclic Sulfur Compounds	-
Organophosphorus Compounds	+
Carbamates	+
Pesticides	+ (6)

(1) Requires pH above 11.
(2) Hydrolysis rates generally high at neutral pH.
(3) Glycols resistant to hydrolysis; Epoxides hydrolyze readily at neutral pH.
(4) Groups are potentially hydrolyzable. Available rate data limited.
(5) Sulfonic Acid esters are hydrolyzable.
(6) Application of base-catalyzed hydrolysis is compound specific.

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SECTION 5

CHEMICAL OXIDATION

Chemical oxidation is a process in which the oxidation state of a substance is increased, which is equivalent to the loss of electrons by the oxidized moiety. Although oxidizing agents most often supply oxygen during the oxidation process, other electron acceptors can be utilized. Examples of chemical oxidation include the oxidation of formaldehyde by hydrogen peroxide:

$$2HCHO + H_2O_2 = 2HCOOH + H_2 \qquad (5\text{-}1)$$

$$HCOOH + H_2O_2 = CO_2 + 2H_2O \qquad (5\text{-}2)$$

or the oxidation of phenol by ozone:

$$C_6H_5OH + 14O_3 = 6CO_2 + 3H_2O + 14O_2 \qquad (5\text{-}3)$$

This section discusses the application of various chemical oxidation processes in treating organic compounds in water and waste treatment, and evaluates their potential application in waste deposit stabilization. The chemical oxidants evaluated in this report, which may be suitable for in situ stabilization of organic wastes, are hydrogen peroxide, ozone, and hypochlorites. The use of these oxidants for treatment of waste and wastewater is well documented. However, very little published information or data from manufacturers was found on the application of chemical oxidation for in situ degradation of organic compounds in waste deposits. Therefore, the evaluation of the in situ application potential must be regarded as generally hypothetical and untested in field situations. Because a single oxidizing agent can oxidize a wide variety of compounds, each at different rates and producing different oxidation products, bench and pilot-scale studies will be required to determine the in situ oxidation rates of the contaminants in question and ensure that undesirable (i.e., toxic) by-products are not generated.

5.1 Hydrogen Peroxide

5.1.1 Properties of Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a weakly acidic, clear colorless liquid, fully miscible with water. It is commercially available in aqueous solution over a wide concentration range. Properties of pure hydrogen peroxide and aqueous hydrogen peroxide at various concentrations are listed in many chemical handbooks, including Kirk-Othmer (1979).

The major chemical reactions and uses of hydrogen peroxide are based on its molecular structure which includes a covalent oxygen-oxygen bond. The principal reaction is oxidation, although some applications involve decomposition, molecular additions, substitutions and reductions. These reactions of hydrogen peroxide can be expressed as:

$H_2O_2 + W = WO + H_2O$ (oxidation) (5-4)
$2H_2O_2 = 2H_2O + O_2$ (decomposition) (5-5)
$H_2O_2 + Y = YH_2O_2$ (molecular addition) (5-6)
$H_2O_2 + RX = ROOH + HX$ (substitution) (5-7)
$H_2O_2 + Z = ZH_2 + O_2$ (reduction) (5-8)

Hydrogen peroxide may react directly or after it has first ionized or dissociated into free radicals. In the presence of catalysts, particularly ferrous and ferric ions, hydrogen peroxide is decomposed to hydroxyl and perhydroxyl radicals. These are very powerful oxidants and are the basis of the Fenton reaction (Dorfman and Adams, 1973) which is used to effect a variety of oxidations. The following equations show the pathways of hydroxyl radical formation:

$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH$ (hydroxyl radical) (5-9)
$Fe^{3+} + H_2O_2 = Fe^{2+} + H^+ + HO_2$ (perhydroxyl radical) (5-10)

Hydrogen peroxide is a moderate strength chemical oxidant compared to chlorine; its advantage is that hydrogen peroxide does not produce unwanted and potentially hazardous chlorinated reaction products. However, the reaction of hydrogen peroxide with high concentrations of some organic and inorganic wastes can be strongly exothermic (heat-producing). Wastes containing amines, cyanides, formaldehyde, phenols, ferrous ion or hypochlorite at much greater than 1000 ppm have shown rapid temperature increases and possible splattering or explosion due to gas evolution.

5.1.2 Oxidation of Organics by Hydrogen Peroxide

Hydrogen peroxide is used in municipal wastewater treatment to control hydrogen sulfide generation, promote BOD and COD reduction, and for bulking in activated sludge plants. In industrial wastewater treatment hydrogen peroxide is used to detoxify cyanide and organic pollutants including formaldehyde, phenol, acetic acid, lignin sugars, surfactants, amines and/or glycol ethers and sulfur derivatives. A wide variety of organic compounds can be oxidized by hydrogen peroxide. These include aldehydes, amines and amides, phenols, various nitrogen and sulfur compounds, aliphatic and aromatic hydrocarbons and others. Table 5-1 lists various chemical classes' reactivity with hydrogen peroxides and any special conditions required (if known).

5.1.3 Application Potential of Hydrogen Peroxide for In Situ Treatment

At the present time, there is no actual field experience upon which to evaluate the potential efficiency of hydrogen peroxide in oxidizing chemical contaminants in waste deposits. As such, laboratory and/or pilot plant studies utilizing the actual waste deposit matrix to study the effectiveness of treatment by hydrogen peroxide would be required prior to any actual usage.

The documented application of hydrogen peroxide in treating different classes of chemical wastes are: aldehydes, phenol, mercaptans, amines, hydroquinones, hydrogen sulfide, cyanide, sulfides and disulfides. In addition hydrogen peroxide is known to react with a wide variety of other organic compounds.

TABLE 5-1

ORGANIC CHEMICAL CLASSES
ABILITY TO REACT WITH HYDROGEN PEROXIDE

	YES	NO	UNKNOWN	COMMENTS
1. Aliphatic Hydrocarbons	x	x		(Saturated alkanes unreactive; unsaturated compounds form epoxides and poly hydroxy compounds).
2. Alkyl Halides	x			
3. Ethers		x		
4. Halogenated Ethers and Epoxides			x	
5. Alcohols	x			Requires Fe^{+2} catalyst; forms acetic acid and CO_2.
6. Glycols, Epoxides	x			
7. Aldehydes, Ketones	x			May require Fe^{+2} catalyst and alkaline conditions (pH 9-11); forms organic acids. Reaction time = minutes.
8. Carboxylic Acids	x			
9. Amides	x			
10. Esters		x		
11. Nitriles	x			Forms amides.
12. Amines	x			Primary amines react to form hydroxylamines, Azo, Azoxy, nitroso and nitro-compounds; secondary amines react to form di-N-substituted (R_2NOH) hydroyxl amines. Reaction time = minutes to hours.
13. Azo Compounds, Hydrazine Derivatives	x			
14. Nitrosamines	x			
15. Thiols	x			May require catalyst.
16. Sulfides, Disulfides	x			May require catalyst; may require low pH, Fe^{+2} catalyst or elevated temperature ($80^{o}C$). dialkyl sulfides (RSR yield sulfoxides; dialkyl disulfides (RSSR) yield sulfonates.
17. Sulfonic Acids, Sulfoxides			x	
18. Benzene and substituted Benzene	x			Requires Fe^{+2} catalyst; forms phenol.
19. Halogenated Aromatic Compounds			x	
20. Aromatic Nitro Compounds	x			Conversion of nitrobenzene to nitrophenyl hydroxylamine reported; requires acetic acid and FE^{+2} catalyst.

TABLE 5-1 (Cont'd)

WASTE CHEMICAL CLASSES
ABILITY TO REACT WITH HYDROGEN PEROXIDE

	YES	NO	UNKNOWN	COMMENTS
21. Phenols	x			Requires Fe^{+2} catalyst and acid conditions (pH=3-5). Forms organic acids which can be completely degraded to CO_2. Reaction time = minutes to hours.
22. Halogenated Phenolic Compounds	x			
23. Nitrophenolic Compounds	x			
24. Fused Polycyclic Hydrocarbons	x			Forms quinones; further oxidation results in ring cleavage.
25. Fused Non-Aramotic Polycyclic Hydrocarbon	x			
26. Heterocyclic Nitrogen Compounds	x			
27. Hetrocyclic Oxygen Compounds	x			
28. Hetrocyclic Sulfur Compounds			x	
29. Organophosphorus Compounds			x	
30. Hydroquinones	x			Requires Fe^{+2} catalyst and acid conditions (pH 3-5); forms organic acids. Reaction time = 30 minutes.
31. Mercaptans	x			Requires alkaline conditions; may require Fe^{+2} catalyst; forms sulfonic acids (RSO_3H) and disulfides (RSSR). Reaction time = 30-60 minutes.
32. Olefins	x			Form epoxy derivatives; further oxidized to glycols or polyhydroxy compounds.

The reactivity of hydrogen peroxide with 29 different classes of chemical wastes, based on the literature search and information provided by the manufacturers of hydrogen peroxide, is indicated in Table 5-1. For efficient oxidation of complex organics, a catalyst such as Fe^{+2} is often required.

It must be recognized, however, that the data presented in Table 5-1 are merely suggestive of potential applications, and that one or more of the following factors may limit the application of hydrogen peroxide as an in situ treatment agent for waste deposits:

1. Hydrogen peroxide may react with explosive force with organic compounds and/or reducing agents. Therefore, careful determination of waste deposit chemical characteristics must be performed, and dilute solutions of peroxide maybe required from the safety standpoint.

2. The potential stability (half-life) of hydrogen peroxide in waste deposits is unknown. Decomposition of the peroxide may occur during transport to or through a deposit.

3. Effective treatment of many organic substances with hydrogen peroxide may require special conditions (pH, temperature or the presence of catalysts) which may be difficult or impossible to attain in a waste deposit.

4. Hydrogen peroxide may react with organic or inorganic substances present in the waste deposit other than the target compounds, greatly limiting treatment efficiency.

5. Treatment with hydrogen peroxide may in some cases result in production of degradation products more toxic than parent compounds (e.g., epoxides and nitrosamines).

6. Compounds strongly sorbed to the solid matrix or insoluble in water may be difficult to treat effectively.

In the event that these potential problems can be overcome at a given site, the use of hydrogen peroxide as an oxidant offers certain advantages, namely:

1. It is available commercially as a liquid in various concentrations.

2. It is miscible in water at all concentrations, simplifying mixing with water on the surface and in the waste deposit.

3. The density and viscosity of dilute hydrogen peroxide solutions are close to those of water, allowing use of standard designs for delivery and recovery systems.

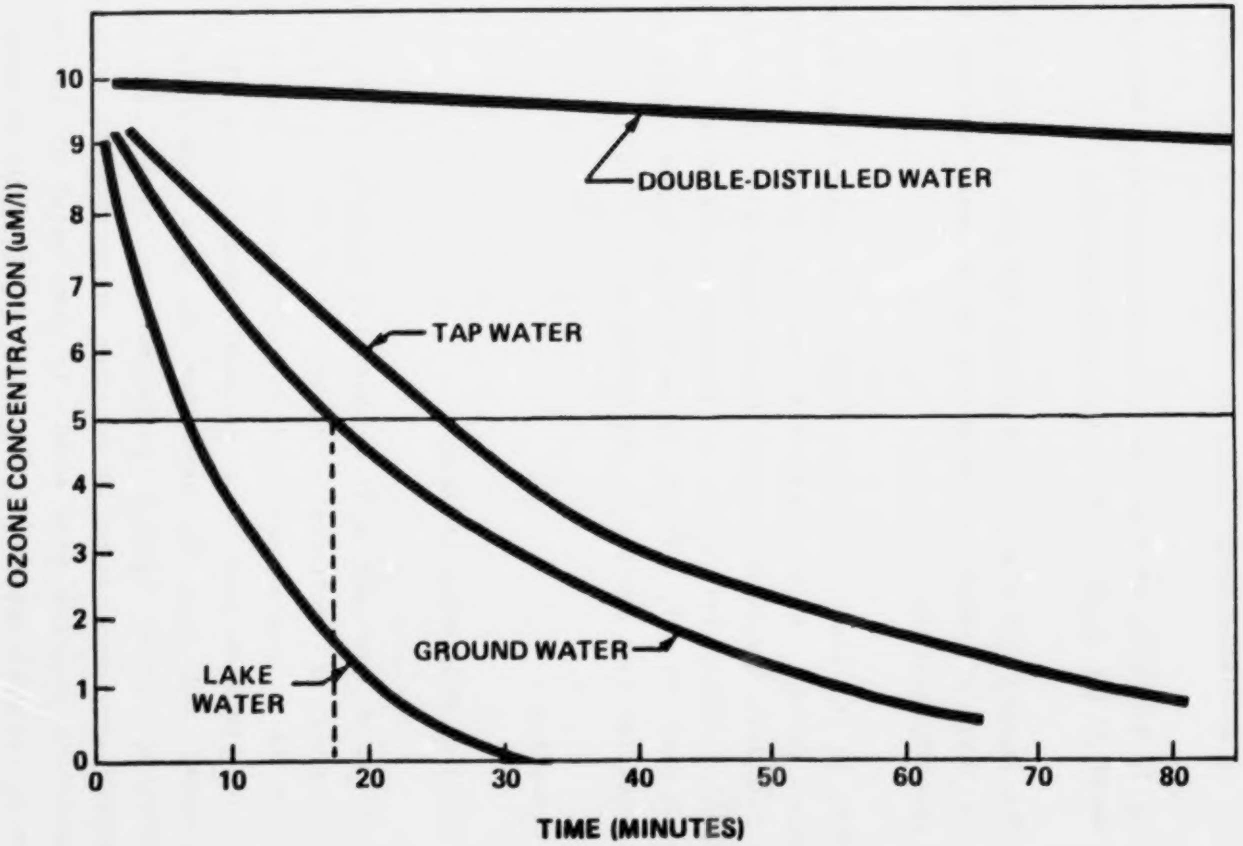
However, in the absence of field information indicating its effectiveness for in situ treatment of waste deposits, hydrogen peroxide can only be considered as a potential treatment reagent whose application awaits further laboratory and field testing before use at existing waste sites can be contemplated. Hydrogen peroxide may, however, be used as an oxygen source to promote aerobic biodegradation (see Section 2 and Wetzel et al., 1985).

5.2 Ozonation

5.2.1 Properties of Ozone

Ozone (O_3), a blue gas with a characteristic odor, is a strong oxidizing agent capable of oxidizing a variety of organic and inorganic compounds. Ozonation is a common method of waste treatment, but it requires certain precautions because ozone is an extremely reactive gas. It cannot be shipped or stored, and must be generated on site immediately prior to its application. Ozone rapidly decomposes to oxygen in aqueous solutions containing impurities (such as organics or particulate matter), although the decomposition proceeds more slowly in pure water or in the gaseous phase. Figure 5-1 illustrates the decomposition of ozone in different water types at $20^{o}C$ ($68^{o}F$). This figure shows that in double-distilled water only 10% of the ozone is decomposed after 85 minutes (an extrapolated half-life of about 9

FIGURE 5-1
DECOMPOSITION RATES OF OZONE IN VARIOUS WATERS (20₀C)



SOURCE: HANDBOOK OF OZONE TECHNOLOGY AND APPLICATIONS, R. RICE AND A. NETZER, 1982 hours), but if organics are present in the water the decomposition rates increase dramatically (half-lives of about 18 minutes in groundwater and less than 10 minutes in some lake waters).

Physico-chemical characteristics of ozone can be found in many chemical handbooks, including Kirk-Othmer (1979) or Masschelein (1982). Its solubility in water is dependent on equilibrium constants as defined by Henry's Law. Impurities in water can have a substantial influence on the solubility of ozone, either increasing or decreasing it.

Table 5-2 summarizes the ability of many waste chemical classes to react with ozone. Mallevialle (1982) has compiled an extensive review of individual reaction by-products and precursors for ozonation of a wide variety of compounds.

5.2.2 Oxidation of Organics by Ozone

Oxidation of organic compounds with ozone can occur along three different pathways. These pathways are (Masschelein, 1982):

- Direct oxidation of the organic compound by ozone,
- Oxidation of the organic by hydroxyl free radicals formed from decomposed ozone, or
- Oxidation reaction induced by interaction between ozone and the solute.

Each of these oxidation pathways will result in different types of end products. Therefore, the specific oxidation mechanism of the organic compounds in question should be known so that undesirable (toxic) compounds are not produced.

Oxidation rates of solutions of organic materials are rapid during the early stages of ozonation, but then the rates slow considerably. This is explained by both the concentrations of readily oxidizable organic materials becoming

TABLE 5-2

ORGANIC CHEMICAL CLASSES

ABILITY TO REACT WITH OZONE

		YES	NO	UNKNOWN
1.	Aliphatic Hydrocarbons			
	saturated		X	
	unsaturated	X		
2.	Alkyl Halides			X
3.	Ethers	X		
4.	Halogenated Ethers and Epoxides			X
5.	Alcohols	X		
6.	Glycols, Epoxides		X	
7.	Aldehydes, Ketones	X		
8.	Carboxylic Acids	X		
9.	Amides			X
10.	Esters	X		
11.	Nitriles			X
12.	Amines	X		
13.	Azo Compounds, Hydrazine Derivatives			X
14.	Nitrosamines			X
15.	Thiols			
16.	Sulfides, Disulfides	X		
17.	Sulfonic Acids, Sulfoxides	X		
18.	Benzene and substituted Benzene	X		
19.	Halogenated Aromatic Compounds	X		
20.	Aromatic Nitro Compounds	X		
21.	Phenols	X		
22.	Halogenated Phenolic Compounds	X		
23.	Nitrophenolic Compounds	X		
24.	Fused Polycyclic Hydrocarbons	X		
25.	Fused Non-Aromatic Polycyclic Hydrocarbons			X
26.	Heterocyclic Nitrogen Compounds			X
27.	Hetrocyclic Oxygen Compounds			X
28.	Hetrocyclic Sulfur Compounds			X
29.	Organophosphorus Compounds	X		

lower and the organic oxidation products of ozonation being more refractory to oxidation. Many compounds which are oxidized slowly by ozone will react 100 to 1,000 times faster in the presence of ultraviolet radiation or ultrasonic energy.

The reaction rate of ozone with organics is also affected by pH. At a high pH the slower hydroxyl free radical reaction will dominate; thus pH can be used to control the reaction rate (USEPA, 1984).

5.2.3 Applications of Ozonation

Ozone has been used in the United States and more extensively in Europe for the treatment of drinking water supplies, municipal wastewater treatment, industrial waste treatment and in a few isolated cases the treatment of contaminated groundwater.

5.2.3.1 Drinking Water Treatment

Unlike chlorination, using ozone as an oxidizing agent for the treatment of potable water does not lead to the formation of undesirable chlorinated organic substances such as trihalomethanes (THM), which are believed to be carcinogens. Ozonation is usually not used in conjunction with chlorination since it has been found that ozonation prior to chlorination increases the formation potential of compounds such as THM (Katz, 1980).

Ozonation of drinking water has been used successfully for the following applications (Rice and Netzer, 1982):

- Bacterial Disinfection
- Viral Inactivation
- Oxidation of Soluble Iron and/or Manganese
- Decomplexing Organically Bound Manganese (Oxidation)
- Color, Taste and Odor Removal (by Oxidation of Organics)
- Algae Removal
- Oxidation of Organics (Phenols, Detergents, Pesticides)

- Microflocculation (Oxidation) of Dissolved Organics
- Oxidation of Inorganics (Cyanides, Sulfides, Nitrites)
- Turbidity or Suspended Solids Removal (Oxidation)
- Pretreatment for Further Biological Treatment (Oxygenation of groundwater or oxidation of complex organics to simpler, more biodegradable compounds).

5.2.3.2 Industrial and Municipal Wastewater Treatment

The major application of ozonation in municipal wastewater treatment has been for disinfection following primary and/or secondary treatment. It has also been successfully used for lowering levels of biochemical oxygen demand (BOD) or chemical oxygen demand (COD); oxidation of ammonia; removal of color, organics, or suspended solids; and odor control.

Ozonation has successfully been used in treatment of industrial wastewaters for the following purposes (Rice and Browning, 1981):

- Oxidation of cyanide in electroplating wastewaters
- Decolorization of dye stuffs
- Removal of phenolic compounds
- Recovery and reuse of spent iron cyanide photoprocessing bleach waters
- Treatment of acid coal mine wastewaters
- Processing wastewaters of mixed ore
- Oxidation of organic waste streams.

Several experiments have been carried out to determine the required doses and effectiveness of ozonation on various organic compounds. The results have been compiled in Katz (1982) and are summarized in Table 5-3. It must be realized that these results can be evaluated only in the context of the experimental design and conditions of the studies reported in Katz (1982). Variables which would alter the experimental results include pH, contact time, ozone dosage, temperature, method of contact, presence of a catalyst, or presence of other competing compounds.

TABLE 5-3

OZONATION OF VARIOUS COMPOUNDS IN WATER

Compound(s)	Initial Concn. (mg/1)	Ozone Dose (mg/1)	Final Concn. (mg/1)	Percent Reduction
Petroleum	10	4.5	0.2 - 0.3	97-98
Gasoline	50	1.29	1	98
		5.1	0.1	99.8
Benzene	200	20	5	97.5
Diethylbenzene	125 - 100	150 - 10	5 - 12.5	88-96
2,2,4-dinitrophenol	50	100	0.35	99.3
	3	17	0.05	98.3
		14	0	100
DDT	0.5	13.8	0.25	50
Malathion	10	3.5	2	80
		9.8	1	90
		2.6	0	100
Methyl-parathion	10	4.5	0.5	95
		9.5	0.1	99
Trichloromethyl parathion	10	8 - 10	0.07	99.3
	0.5 - 1	3.5 - 4.5	0	100
Dinitro-orthocresol	10	5 - 6	0	100

TABLE 5-3 (Cont'd)

OZONATION OF VARIOUS COMPOUNDS IN WATER

Compound(s)	Initial Concn. (mg/l)	Final Concn. (mg/l)	Percent Reduction
Methanol	2000	160	92
Ethanol	1000	90	91
Isoamyl alcohol	1000	80	92
Glycerine	1000	0	100
Hydrazine	100	0	100
Carbon Disulfide	100	0	100
Hydrogen Sulfide	10	0	100
Phenol	100	0	100
o-Cresol	100	0	100
Hydroquinone	100	0	100
Salicyclic Acid	100	0	100
Gasoline	1000	0	100
Benzene	500	0	100
Toluene	500	0	100
Xylene	500	0	100
Acetone	100	30	70

5.2.3.3 Groundwater Pollution Abatement

There are very few cases in which ozonation has been used for groundwater pollution abatement. The most likely use of ozone in this context would be for treatment of contaminated groundwater which has been pumped to the surface, or as an oxygen source for biodegradation. A case history of the use of ozonation for in situ treatment of contaminated groundwater in Karlsruhe, West Germany was reported by Nagel (1982) and Rice (1984).

A municipal well field had been contaminated by hydrocarbons from a nearby railway yard to the north and cyanides from a chemical waste disposal site to the south (Figure 5-2). The well water had high turbidity, one well had elevated cyanide concentrations, and oxygen and nitrate were totally consumed by the contaminants' COD. As a result, two of the four wells in the well field had been closed and the remaining two were threatened. To protect the aquifer against further spread of the contaminants and decline in water quality, an ozone treatment process was developed.

Water from the well contaminated by hydrocarbons was pumped from all levels of the aquifer to a depth of 25 meters (82 ft). Ozone was produced on site from dry air at a concentration of 25 g/m^3 (0.0016 lb/ft^3) and was introduced to the contaminated groundwater by a static tube mixer, where the organics reacted in a bubble column and the ozone decomposed to oxygen. The water was then returned to five fully-penetrating infiltration wells at a rate of 100 m^3/h (26,420 gallons/hr). Figure 5-3 illustrates the water flow diagram for the ozonation process.

The oxygenated recharge water was recycled via the municipal wells after 30 to 40 days retention in the aquifer. This contact time was sufficient to reduce the dissolved organic carbon (by biodegradation) from 3.5 mg/l to 1.5 mg/l in the most heavily polluted well within about 2 months after the start-up of ozonation. As a result the dissolved oxygen content of the groundwater rose to several mg/l and biological activity within the aquifer increased. The water quality was improved sufficiently to allow the well field to remain in operation.

FIGURE 5-2
CITY WATERWORKS
KARLSRUHE WEST GERMANY

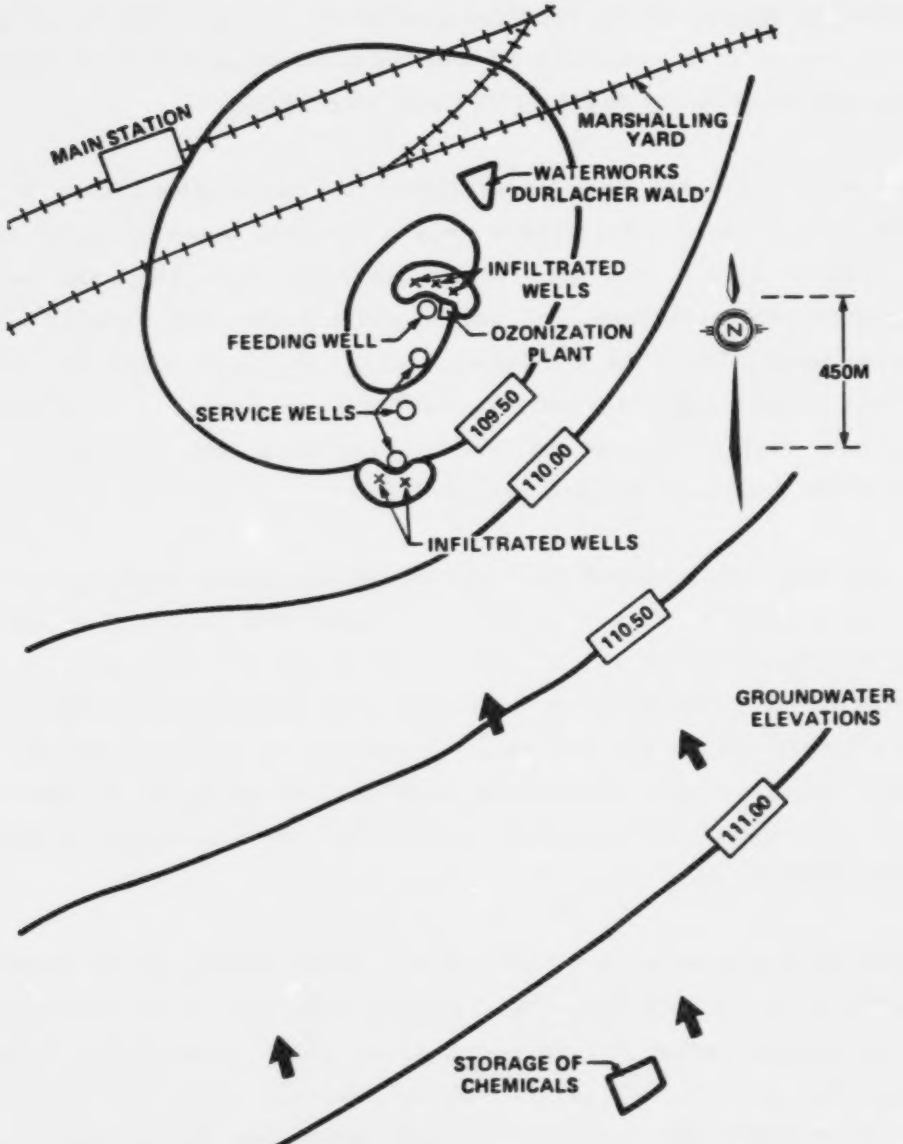
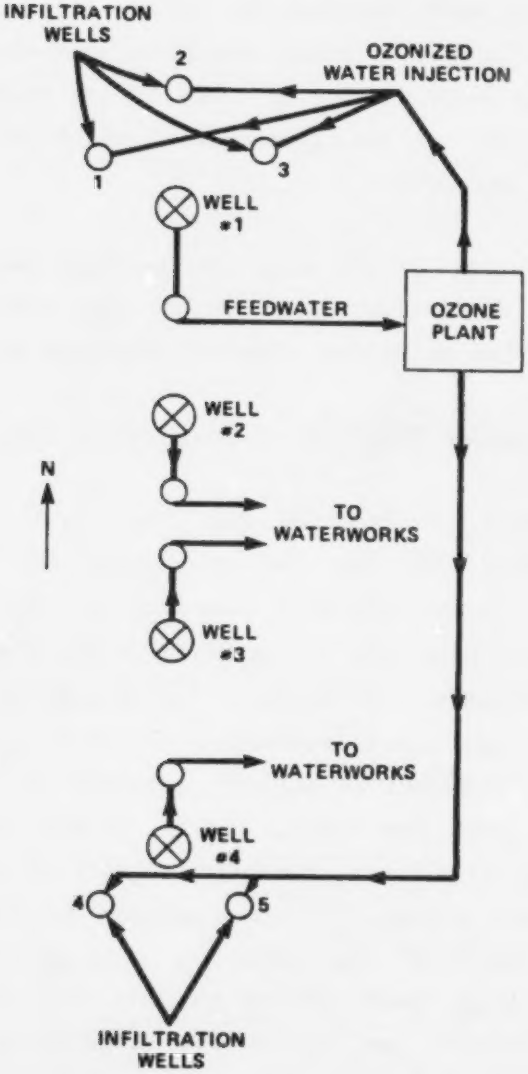

MAIN STATION
MARSHALLING YARD
WATERWORKS 'DURLACHER WALD'
INFILTRATED WELLS
FEEDING WELL
OZONIZATION PLANT
SERVICE WELLS
INFILTRATED WELLS
109.50
110.00
110.50
111.00
N
450M
GROUNDWATER ELEVATIONS
STORAGE OF CHEMICALS

FIGURE 5-3
BASIC FLOW DIAGRAM FOR OZONATION OF GROUND WATER AT KARLSRUHE


INFILTRATION WELLS
2
OZONIZED WATER INJECTION
1
3
WELL #1
FEEDWATER
OZONE PLANT
WELL #2
N
TO WATERWORKS
WELL #3
TO WATERWORKS
WELL #4
4
5
INFILTRATION WELLS

The application reported in this case history diverges somewhat from strictly in situ treatment for the following reasons:

- The groundwater was collected and ozonized conventionally (above ground) to reduce the organic content.

- The ozonized water improved the quality of the recharge water and the groundwater both as a direct result of oxidation of organics by ozone and because decomposition of ozone in the recharge water raised the oxygen content of the groundwater, which in turn promoted native biological activity.

It should be noted that by the time the recharge water left the ozonation plant, it contained no residual ozone but had high concentrations of dissolved oxygen. There was thus no in situ chemical oxidation of organics by the ozone.

5.2.4 Application Potential of Ozone for In Situ Treatment

As illustrated above, ozonization has many applications for water and wastewater treatment, and in some instances for groundwater pollution abatement. In no cases, however, have any of the reported applications involved the direct injection of ozonized water into a waste deposit to oxidize organic materials. Furthermore, the literature survey did not reveal any studies to evaluate the effectiveness of subsurface (in situ) ozonation. The only study of the effect of soil on oxidation of organics using ozone is an experiment with pesticides (Katz, 1980). It was found that the oxidation proceeds rapidly in clean water, but significantly slower when humic materials or soil particles are present. It was suggested in this study that dissolved organics may be adsorbed onto humic or soil materials and become more resistant to oxidation. These results indicate that ozonation in soil may be difficult, and laboratory and pilot-scale experimentation simulating the in situ conditions will be necessary.

It is particularly important to accurately characterize the waste to be ozonized and to perform tests on that specific mixture of compounds for two reasons. First, various organic compounds in aqueous solution may compete for ozone in the oxidation process, since ozone's oxidizing action is non-specific. This could result in acceptable removal of one compound, no removal or very slow removal of another compound of equal concern, or removal of non-toxic natural soil organics but no removal of the more refractory organics of concern. In addition, it is important to design sufficient oxidant into the process to acomplish the amount of oxidation desired. Secondly, the mechanisms of oxidation of the organic compounds originally present must be understood in order to evaluate what oxidation by-products might be formed. Some compounds are oxidized first to intermediates which are more toxic than the starter materials, before being further oxidized to innocuous compounds. An example of this would be the ozonation of the pesticides parathion and malathion, which produces paraoxon and maloxon, respectively (USEPA, 1984). These intermediates are more toxic than the starter materials, but continued ozonation degrades the oxon intermediates. Other examples of toxic byproducts include the ozonation of dimethylhydrazine, 2-hydroxyethylhydrazine and benzidine, which produce mutagenic compounds of varying stability.

Much is still unknown about the mechanism of formation and chemical characteristics of intermediate products. A better understanding of the chemistry of the materials to be oxidized would be necessary to determine the treatability potential of a waste deposit, and to properly design the ozonation system. The major problem with in-situ treatment using ozonation, however, seems to be the rapid decomposition of the ozone in aqueous solution. The half-life of ozone in natural waters is about 10-25 minutes, which is insufficient for delivery or significant contact time when introduced into the soil - the ozonized solution would probably decompose before it reaches the waste deposit. For these reasons, the in situ chemical oxidation of waste deposits using ozone does not appear to be promising.

5.3 Hypochlorites

5.3.1 Properties of Hypochlorites

Hypochlorites as a chemical class are the reaction products of chlorine with an alkali. They are used principally as a means of delivering chlorine without the necessity of handling pure chlorine as a liquid or gas. Hypochlorites are strong oxidizing agents (stronger than hydrogen peroxide) and are almost always used in aqueous solution. The two most common forms of hypochlorite produced commercially are calcium hypochlorite ($Ca(OCl)_2$) and sodium hypochlorite (NaOCl). Sodium hypochlorite is usually produced on a commercial scale in two strengths, 5.25 wt% (household liquid bleach) and 13.03 wt% (commercial strength bleach). Calcium hypochlorite is produced commercially in a form containing about 70% available chlorine. Other hypochlorites used occasionally include barium, lithium and alkyl forms; these are not produced commercially due to poor stability and/or price considerations.

The three basic mechanisms for the reaction of chlorine with an organic compound are addition, substitution and oxidation. Addition and substitution (chlorination) result in the production of chlorinated organic compounds such as trihalomethanes (THM) which, in most cases, are undesirable. The oxidation reaction is the principal waste effluent treatment mechanism but is effective only for a limited number of organic compounds (USEPA, 1979).

In strong solutions at low pH, the chlorination reaction predominates. In weakly acidic solutions the oxidation reaction is primary. The treatment of phenols by hypochlorite provides an example of both reactions. Mono-, di- and tri- substituted phenols are readily formed in solution. These chlorophenols are subsequently degraded to aliphatic acids by excess hypochlorite in an oxidation reaction (Eisenhauer, 1964). Table 5-4 summarizes the ability of various waste chemical classes to react with hypochlorites.

TABLE 5-4

ORGANIC CHEMICAL CLASSES
ABILITY TO REACT WITH HYPOCHLORITES

	YES	NO	UNKNOWN	COMMENTS
1. Aliphatic Hydrocarbons	X			Possible chlorination and formation of chloramines
2. Alkyl Halides	X			Chlorinated product possible
3. Ethers			X	
4. Halogenated Ethers and Eposides			X	
5. Alcohols	X			Forms alkylhypochlorites, hazardous and explosive
6. Glycols, Epoxides			X	Used in preparation of Epoxides and Glycols from Halohydrin
7. Aldehydes, Ketones	X			Reaction of acetaldehyde yielding Chloroform ($CHCl_3$)
8. Carboxylic Acids	X			Chlorinated byproducts possible
9. Amides	X			Forms chloramines, hydrolysis of C-N bond, possible NCl_3 formation
10. Esters		X		Will not react unless unsaturated bonds are available for chlorohydrin formation
11. Nitriles		X		Will not react unless unsaturated bonds are available for chlorohydrin formation
12. Amines	X			Forms chloramines
13. Azo Compounds, Hydrazine Derivatives	X			Forms chloramines
14. Nitrosamines	X			Forms chloramines
15. Thiols			X	
16. Sulfides, Disulfides	X			Sulfides oxidize to sulfoxides without forming sulfones
17. Sulfonic Acids, Sulfoxides		X		
18. Benzene, Substituted Benzene	X			Forms chlorinated aromatic
19. Halogenated Aromatic Compounds	X			Forms chlorinated aromatic, possible oxidation
20. Aromatic Nitro Compounds	X			Forms chlorinated aromatic or chloramine
21. Phenols	X			Forms chlorinated phenols, oxidized to aliphatic acid

TABLE 5-4 (Cont'd)

WASTE CHEMICAL CLASSES AND THEIR
ABILITY TO REACT WITH HYPOCHLORITES

	YES	NO	UNKNOWN	COMMENTS
22. Halogenated Phenolic Compounds	X			Oxidized to aliphatic acid
23. Nitrophenolic Compounds	X			Chlorination of aromatic ring
24. Fused Polycyclic Hydrocarbons (PNA's)	X			Chlorinated and oxidized products (e.g., phenols and quinolines)
25. Fused Non-Aromatic Polycyclic Hydrocarbons	X			
26. Heterocyclic Nitrogen Compounds	X			Chlorinated product formed
27. Heterocyclic Oxygen Compounds	X			Chlorinated product formed
28. Heterocyclic Sulfur Compounds	X			Chlorinated product formed
29. Organophosphorous Compounds	X			

5.3.2 Treatment Applications of Hypochlorites

The major uses of hypochlorite include disinfection of potable water supplies and sewage effluents, control of algae and biofouling organisms, and bleaching of textiles and pulp and paper products. Hypochlorite has had some usage in industrial waste treatment, primarily as an oxidizing agent for cyanide and ammonium sulfide/sulfite wastes. Other uses include taste and odor control (e.g., by oxidation of reduced sulfur or chlorophenols), and removal of reduced iron and manganese species in water (White, 1978).

Chlorine substitution and addition appear to be the most common reactions between chlorine and organics in aqueous solution. Only in a few cases do these reactions proceed beyond this stage, in which they may be considered "oxidative degradations". Thus treatment of organic chemicals in wastewater using hypochlorite appears to have limited potential because the intermediate products are often at least as toxic as the original waste material. This is also true for treatment of drinking water supplies, where THM are reportedly formed from humic acids and other naturally-occurring organic materials (Jolley et al., 1978; Stevens et al., 1978; Rock, 1980).

The production of numerous chlorinated byproducts in waters treated by chlorination has been reported at low concentrations of chlorine addition, typical of municipal water and wastewater drinking effluents. Carlson and Caple (1978) reported the substitutive chlorination of phenol, anisole, acetanilide, and toluene under acid conditions, and Snider and Albey (1980) reported the chlorination of biphenyl to mono- and dichlorinated biphenyls, although the rate of reaction was slow above pH 6.2. Bieber and Trehey (1983) reported formation of dichloroacetonitriles through chlorination of natural waters. Both chlorinated and oxidation byproducts (including phenols and quinones) result from chlorination of polynuclear aromatic materials (Liukonnen et al., 1983). Ghanbari et al. (1983) reported incorporation of chlorine into fatty acids, fatty acid esters and triglycerides.

Increased chlorine doses and contact times can be expected to increase formation of chlorinated byproducts. Heavy chlorination (2000 - 4000 ppm of hypochlorite) of municipal wastewater has been reported by Glaze et al. (1978) to result in substantial increases in chlorinated byproducts. Under these conditions, chlorinated byproducts were formed from non-activated substances (e.g., benzene, toluene, benzyl alcohol) which are generally not observed as byproducts of chlorination at lower doses.

Disinfection with chlorine is well established as a public water supply treatment but the utility of hypochlorite as an oxidant for organic substances in water and wastewater remains doubtful. The only organic wastes that have been treated successfully by oxidative degradation with hypochlorites are phenols and chlorinated phenols. The degradation mechanism leads to the formation of aliphatic acids by cleavage of the aromatic ring. Evidence of other successful organic waste stream treatments by oxidative degradation remains extremely limited.

An important application of hypochlorite oxidation for inorganic waste is that of cyanide waste stream treatment. Cyanide is first oxidized to the less toxic cyanate and then to harmless bicarbonates and nitrogen. This process is capable of achieving an efficiency of 99 percent.

5.3.3 Potential for In Situ Treatment of Waste Deposits Using Hypochlorite

The principal uses of chlorination have been for biological treatment (disinfection) of water, wastewater, sewerage and for cleaning swimming pools. The potential use of hypochlorites (in aqueous solution) for in situ treatment of organic wastes is, at best, extremely limited because the chief products of chlorination are usually undesirable chlorinated organics (Table 5-4). The greatest potential use of chlorination for organic waste treatment resides with phenols and phenolic compounds, where documented oxidative degradation to aliphatic acids has been achieved, or with cyanides (see below). However, control of conditions in a waste deposit to achieve this degradation would be difficult. This information indicates that, except for some specific situations, use of aqueous solutions of hypochlorites is not generally adviseable for in-situ treatment of organic chemicals due to the possible formation of chlorinated organics, as well as the lack of available information on in-situ treatment using hypochlorites.

5.3.3.1 In Situ Oxidation of Acrylonitrile Using Sodium Hypochlorite

A freight train derailment in Ohio led to the spillage and burning of 31600 liters (8360 gallons) of acrylonitrile (CH_2CHCN) (Harsh, 1978). Following the initial cleanup it was decided to oxidize the remaining acrylonitrile in in surface ponds and soils by first raising the pH of the contaminated area above 10 using lime, and oxidizing the cyanide portion of the acrylonitrile molecule using sodium hypochlorite (HTH). The reaction would proceed in three stages (Harsh, 1978):

1) $CN^- + HOCl = CNCl + OH^-$
2) $CNCl + 2OH^- = CNO^- + Cl + H_2O$
3) $2CNO^- + 3OCl^- + H_2O = 2CO_2 + N_2 + 3Cl^- + 2OH^-$

A total of 4360 kg (9600 lbs) of lime was spread over the area first to raise the pH. Then a water solution containing 410 kg (900 lbs) of HTH was sprayed over the area, and an additional 180 kg (400 lbs) of HTH was applied to acrylonitrile pools (Harsh, 1978). Workers were forced to wear gas masks because of strong chlorine gas fumes. Subsequent monitoring indicated no residual acrylonitrile (Harsh, 1978).

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SECTION 6

APPLICATION AND DESIGN OF SYSTEMS TO ACCELERATE STABILIZATION OF WASTE DEPOSITS

6.1 Introduction

Federal (CERCLA) and state hazardous waste programs to date have focused primarily on the need to identify uncontrolled waste deposits, perform remedial investigations (RIs) to assess the nature and extent of threats presented by these deposits, and undertake immediate remedial measures (IRMs), if necessary, to reduce significant public health threats. The next step in waste deposit remediation, long term mitigation of the waste hazard, has until recently consisted predominantly of containment or excavation and off-site management rather than waste treatment or detoxification at the site. Currently, however, attention is being directed to the performance of feasibility studies (FS) on the potential for in situ stabilization of waste deposits (USEPA, 1984a; USEPA, 1985).

The purpose of this report is to present a systematic review of the potential for in situ stabilization of organic waste deposits. Of utmost importance, it must be remembered that:

- The process technologies for in situ treatment have not been established with confidence. In fact, there is very little documentation of field pilot and full-scale testing in this regard with the exception of biodegradation (information gaps with regard to in situ stabilization are discussed further in USEPA, 1984a).

- The delivery/recovery systems for implementing in situ treatment methodologies can probably be adapted from other existing applications (i.e., wastewater treatment, ground water collection and aquifer management, construction site dewatering, subsurface injection of waters and grouts, irrigation engineering). However, these applications have had limited objectives, have been utilized in benign applications where the implications of threat to public health, welfare and the environment have not been an issue, and have generally not been tested for in situ waste treatment.

- The feasibility and cost-effectiveness of conceptual delivery/treatment/recovery systems have in general not been established (except for a few cases such as the Biocraft Site, described in Section 6.5), especially as these relate to achieving different degrees of remediation within required time frames.

This report must therefore be viewed only as a guidance document with respect to potential technologies for in situ waste stabilization as they currently exist, that is in their conceptual or developmental stage. The following sections describe the steps required for the evaluation of biodegradation, surfactant-assisted flushing, hydrolysis and oxidation applications for in situ treatment of wastes. In addition, a methodology for selection of delivery and recovery systems is presented. The processes of defining the remedial objectives for a site and selection of possible alternatives (including in situ stabilization), which is a prerequisite in the National Contingency Plan (NCP) procedure (USEPA, 1985) before in situ stabilization can be considered, and of comparing alternatives and selection of the remedial action(s) to be implemented, are described in A.D. Little (1983), USEPA (1984a), and Repa and Kufs (1985).

6.2 Remedial Investigation

Definition of the nature and extent of the wastes at the site, and the geohydrologic and geochemical conditions of the site, is a necessary prerequisite to the evaluation of the feasibility of any remedial approach (in situ stabilization or any other actions). These data are usually collected during the remedial investigation (RI) stage of site evaluation, prior to the feasibility study (FS) stage, during which the evaluation of in situ stabilization technologies described in this report would take place.

The extent of contamination is determined from the area and depth occupied by the wastes, and the chemical composition and concentrations of the various waste components. The waste forms (free liquid, solid, contaminated soils) should also be determined. This information may be available from the site operator/owners or from regulatory agencies; otherwise a site investigation will be required to obtain or confirm the information. Geohydrological parameters (such as site stratigraphy and topography, soil types, permeabilities, infiltration rate, and groundwater depth and flow direction), as well as meteorological and local land use characteristics, should be determined as required to fully characterize the site for the design of the necessary delivery/recovery systems. The physical and chemical characteristics of groundwater, which can affect the feasibility of the treatment technique, should also be determined. These parameters should include pH, temperature, and inorganic and organic chemical composition. In addition, a risk assessment would be required to determine the potential routes of exposure and risk to humans and the environment, and therefore the levels to which remediation would be required. Assessment of waste, soil and groundwater characteristics as well as local site conditions is further described in USEPA (1984a) and Repa and Kufs (1985).

6.3 Feasibility Study

After the site conditions and contaminant characteristics have been defined during the Remedial Investigation, a Feasibility Study, in which the various in situ stabilization methods are evaluated, can be undertaken (USEPA, 1984a). The first step is to evaluate, using the information presented in this report, whether any of the contaminants present may be susceptable to in situ biodegradation, surfactant-assisted flushing, hydrolysis or chemical oxidation. Table 6-1 summarizes the potential applications of these methods to waste materials. If any of these methods appear to be promising, the method(s) are further investigated as described in the following subsections.

TABLE 6-1

POTENTIAL APPLICATIONS OF TREATMENT METHODS TO WASTE CONTAMINANTS

Chemical Class	Treatment Technology				
	Biodegradation	Base-Catalyzed Hydrolysis(1)	Oxidation(2)	Water Flushing(3)	Surfactant Flushing(3)
Aliphatic Hydrocarbons	+	-	+	-	+
Alkyl Halides	+	+	?	-	?
Ethers	+	-	?	-	+?
Halogenated Ethers and Epoxides	+	+	?	?	?
Alcohols	+	-	+	+	-
Glycols/Epoxides	+	-/+	+	?	?
Aldehydes, Ketones	+	-	+	+?	-?
Carboxylic Acids	+	-	+	?	?
Amides	+	+	+	?	?
Esters	+	+	?	?	?
Nitriles	+	+	+	?	?
Amines	+	+	+	+?	-?
Azo Compounds, Hydrazine Derivatives	+	-	+	?	?
Nitrosamines	+	-	+	?	?
Thiols	+	-	+	?	?
Sulfides, Disulfides	+	-	+	?	?
Sulfonic Acids, Sulfoxides	+	?	?	?	?
Benzene & Substituted Benzene	+	-	+	-	+
Halogenated Aromatic Compounds	+	-	?	-	+
Aromatic Nitro Compounds	+	-	+	?	?
Phenols	+	-	+	+	-
Halogenated Phenolic Compounds	+	-	+	?	?
Nitrophenolic Compounds	+	-	+	?	?
Fused Polycyclic Hydrocarbons	+	-	+	-	+
Fused Non-Aromatic Polycyclics	+	-	+	-	+
Heterocyclic Nitrogen Compounds	+	-	+	-	+?
Heterocyclic Oxygen Compounds	+	-	+	-	+
Heterocyclic Sulfur Compounds	+	-	?	-	+
Organophosphorus Compounds	+	+	?	?	?
Carbamates	+	+	?	?	?
Pesticides	+	+	?	?	?

(1) Based upon calculated half-lives for hydrolysis of representative compounds at pH 9 to 11.

(2) Based upon literature for oxidation of chemicals in water and wastewater by hydrogen peroxide.

(3) Based upon aqueous solubility and octanol/water partition coefficient (K_{ow}) of representative compounds. Specific application will depend on solubility and K_{ow} for specific compounds.

+ = can be used
- = cannot be used
? = Further research necessary
-? = Probably cannot be used
+? = Probably can be used

There are certain potential problems or concerns which must be addressed when considering any in-situ treatment system. These problems must be analyzed on a site-specific and treatment-specific basis, and can only be discussed in general terms here. Primary among these is the problem of waste heterogeneity, both with respect to irregular contaminant distribution and inhomogeneous waste/soil physical properties (hydraulic conductivity, stratification, depth to water table). This may lead to incomplete saturation of the waste deposit and poor or incomplete exposure of the contaminants to the reactant solution. Another potential problem relates to excessive dilution or attenuation of the reactant solution, which may occur if large volumes of water are required to saturate the deposit, if groundwater flow through the deposit is rapid, or if the delivery system does not apply the reactant directly to the waste deposit (e.g., by using injection wells) so that it is attenuated or diluted during passage through overlying or upgradient soils.

All materials to be used in the delivery and recovery systems, particularly pipes, pump internal parts, and liners, must either be tested or checked with the manufacturer or available literature for compatibility with the treatment solution(s) and waste components. This should take place during the bench scale treatability or field pilot study steps. Potential materials that can be used for delivery/recovery piping include polyvinyl chloride (PVC), stainless steel, carbon steel, polyethylene, styrene rubber, ABS (acrylonitrile-butadiene-styrene), concrete, fiberglass, bituminized fiber, or clay. It is probable that one or more of these materials will meet the chemical and physical requirements of the specific application.

Finally, it must be recognized that the waste may consist of a mixture of compounds with varying treatability by these methods; thus more than one in situ treatment method may be required. In addition, other remedial actions (such as excavation and treatment at the surface) may be required to treat the concentrated source material, while in situ methods are used to treat the more extensive, but lower concentration, plume. Furthermore, a particular technique (e.g., hydrolysis) may detoxify certain compounds, but alter others into more toxic forms or produce toxic intermediate compounds or by-products. These possibilities must be carefully evaluated during the feasibility study on a compound-by-compound basis.

6.3.1 Evaluation of Biodegradation for In Situ Stabilization of Waste Deposits

A systematic approach is developed in this section, based on the discussion presented in Section 2 and data in Appendix A, to evaluate the utilization of biodegradation as an in situ method to renovate waste piles or deposits. As shown in Figure 6-1, this approach consists of eight steps, each of which is described below.

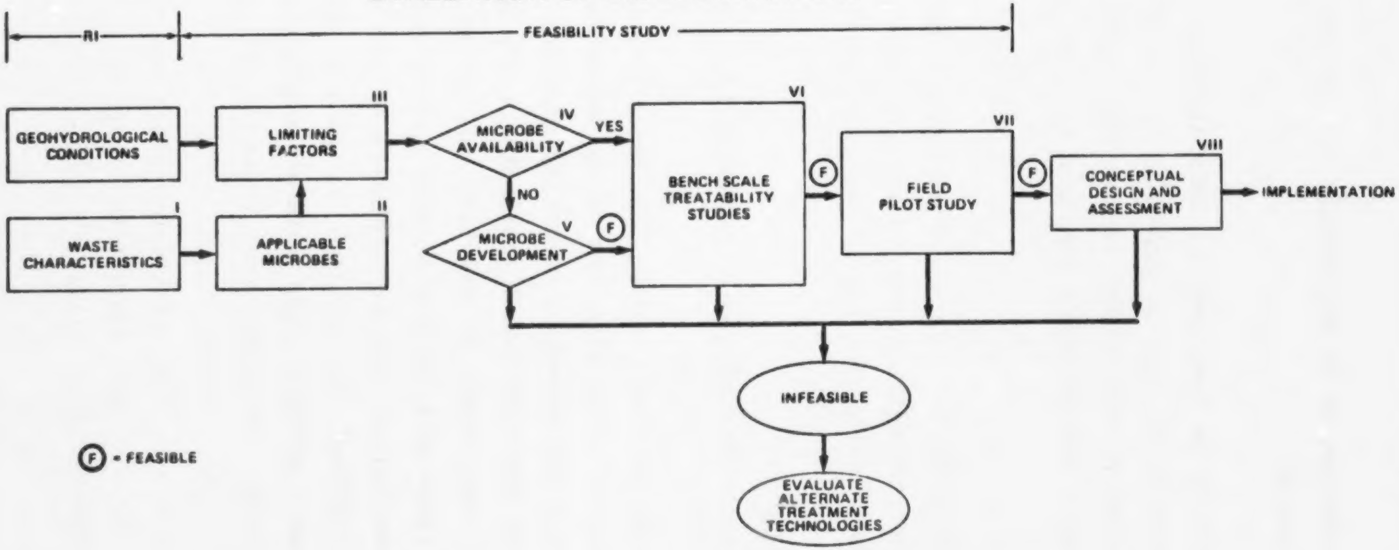
The preliminary steps are to understand the nature and extent of wastes at the site, the site geohydrologic parameters and groundwater and soil chemistries. These steps are performed during the RI (see Section 6.2).

6.3.1.1

Determine Nutritional and Biological Characteristics of the Wastes (Step I)

This step should be performed during the waste characterization step of the RI. The objectives of this step are 1) to determine certain environmental factors which affect the selection of proper microbes for in situ renovation; 2) to quantify the basic nutrients available at the site for supporting the selected microbes (see Steps II and III; and 3) to identify the microbial community at the waste site so that certain native microbes may be considered for use in site remediation, and any predators of the selected microbes may be identified. The physical and chemical parameters which should be measured are pH, temperature, porosity, and moisture content of the soil, and redox potential, phosphorus, nitrogen and trace metal concentrations in the groundwater.

FIGURE 6-1
EVALUATION OF BIODEGRADATION


RI
FEASIBILITY STUDY
GEOHYDROLOGICAL CONDITIONS
WASTE CHARACTERISTICS
I
LIMITING FACTORS
III
APPLICABLE MICROBES
II
MICROBE AVAILABILITY
IV
YES
NO
MICROBE DEVELOPMENT
V
F
BENCH SCALE TREATABILITY STUDIES
VI
F
FIELD PILOT STUDY
VII
F
CONCEPTUAL DESIGN AND ASSESSMENT
VIII
IMPLEMENTATION
INFEASIBLE
EVALUATE ALTERNATE TREATMENT TECHNOLOGIES
F = FEASIBLE

In addition, if the wastes are in solid or particulate form (e.g., spent resins), permeabilities of these wastes should also be determined via in situ methods or in the laboratory as appropriate. These data are needed for designing the delivery/recovery systems (see Section 6.4) for transporting microbes, water, nutrients, and oxygen to the wastes.

6.3.1.2 Identify Potentially Applicable Microbes (Step II)

Certain microbes potentially capable of degrading the organic materials in the waste deposit can be identified by review of Appendix A of this report. An updated literature review should also be performed on biodegradation of these organics because of the rapidly-evolving nature of this field. If no single species of microbes can be identified, this evaluation should continue on to Step V (i.e., skip Steps III and IV).

6.3.1.3 Assess Presence and Absence of Limiting Factors (Step III)

In this step, the optimum growth conditions of the potentially-applicable microbes identified in Step II are compared with waste site conditions determined in Step I. Through these comparisons, the physical and chemical factors at the waste site capable of limiting the growth of the microbes (e.g., oxygen availability - surface vs subsurface or aerobic vs anaerobic; pH - acidic vs alkaline; temperature; presence of toxins; nutrients) can be identified. If these limiting factors cannot be corrected (e.g., adding oxygen, buffer solution, fertilizers, etc.), the microbes identified would have to be eliminated from further consideration.

6.3.1.4 Availability of Microbes (Step IV)

Commercial firms which culture specialized microbial strains for biological treatment of specific organics, or which enhance and adapt native microbes to more efficiently degrade the identified organics, should be contacted to determine the commercial availability of the microbes identified in Step II, or any new microbial strains capable of degrading the wastes. If such microbes are available, this evaluation should move on to Step VI; otherwise the research described in the following step would be needed to develop microbes capable of biodegrading the identified organics.

6.3.1.5 Conducting Research to Develop New Microbial Strains (Step V)

Microbes with the required characteristics may be developed by use of native microflora (identified in Steps I and II), adapted microorganisms, or genetically modified microbes (i.e., through specific gene mutation or genetically assisted molecular breeding). These microbes should be developed for optimal growth at the specific physical and chemical conditions at the waste site as well as the waste concentrations. To develop new microbial strains it will be necessary to employ trained microbiologists or to utilize the services of a firm or university having the specialized expertise required to develop new strains. Such testing may extend well beyond the expertise usually associated with sanitary engineering applications to municipal sewage treatment systems.

The microbes should be tested to determine whether they can effectively degrade the identified organics. The potential for inhibition of microbial growth by the wastes or the site environment should also be evaluated. If microbes which are effective under in situ conditions can be developed, this evaluation should continue to the next step (Figure 6-1). Otherwise, this evaluation should be terminated, and alternative in-situ treatment methods should be investigated.

The potential for adverse environmental impact of the selected microbes (either enhanced native microbes, adapted microbes, or new genetically engineered strains) should be analyzed. Such impacts may include, but not be limited to, groundwater contamination and subsequent human health effects, and changes in the local microbial community and soil conditions so that the reclaimed land may not be capable of sustaining the original vegetation. The most suitable microbes for in situ biodegradation of organics are those which produce no health impact to human beings, and are very specific for the identified wastes (that is, they would not degrade other organics in the soil or compete for nutrients with other microorganisms, and they will expire when the wastes are no longer available).

6.3.1.6 Laboratory (Bench Scale) Simulation Tests (Step VI)

Those microbes which are acceptable based on the risk analysis and assessment of in situ limiting factors would advance to laboratory simulation tests. The purpose of these tests is to determine the maximum biodegradation rate which can be achieved under simulated in situ conditions. In this simulation, proper modification of site conditions to improve the biodegradation rate should also be considered. These modifications may include:

- Addition of buffers to adjust pH,
- Addition of fertilizers to provide adequate nutrients,
- Addition of emulsifiers to solubilize the wastes,
- Addition of water to adjust the moisture content, and
- Addition of oxygen to support the aerobic microbes.

Based on the results of these tests, the following parameters should be determined for the maximum biodegradation rate:

- Microbial concentration,
- Substrate concentration,
- Buffer concentration and dosing rate (if needed),
- Nutrient concentration and dosing rate (if needed),
- Emulsifier concentration and dosing rate (if needed),
- Water dosing rate (if needed), and
- Oxygen concentration and dosing rate (if needed).

These data are required for conducting on-site pilot tests. In addition, any end products and side reaction products in the soil or in the recovered solution should be identified to check whether the waste organics are in fact biologically degraded, and whether any other toxic intermediates or by-products are generated, which would require additional treatment. Any gases generated should also be quantified, especially for the case of subsurface waste deposits, which may require venting.

The simulation tests for surface waste piles may be performed as beaker or simple microcosm tests. For the case of subsurface waste deposits, the simulation tests can be performed as simple column tests or as more complicated microcosm systems to better represent the waste site conditions.

If more than one microbial strain has promising characteristics, the simulation tests should be performed first on the strain which produces higher degradation rates and can grow better under the waste site conditions. Whether the other strains should be tested will depend on the schedule and budget of a given in situ renovation project.

6.3.1.7 Onsite Pilot Test (Step VII)

In this step, a representative plot at the waste site (either surface pile or subsurface deposit) should be selected for conducting a pilot test to confirm the results obtained from the laboratory simulation tests (mainly, the maximum biodegradation rate and its associated physical and chemical requirements). In addition, the spray systems and tilling operation (for the case of surface piles) or delivery/recovery systems (for the case of subsurface deposits) designed for this pilot test would provide design and operational guidance for the full-scale treatment facility. A further description of pilot-scale testing, including sampling, analysis and monitoring methodologies, is provided in USEPA (1984a) and references therein. The delivery/recovery system which may be used for this application are described in Section 1 of this report.

6.3.1.8 Facility Conceptual Design and Cost-Effectiveness Assessment (Step VIII)

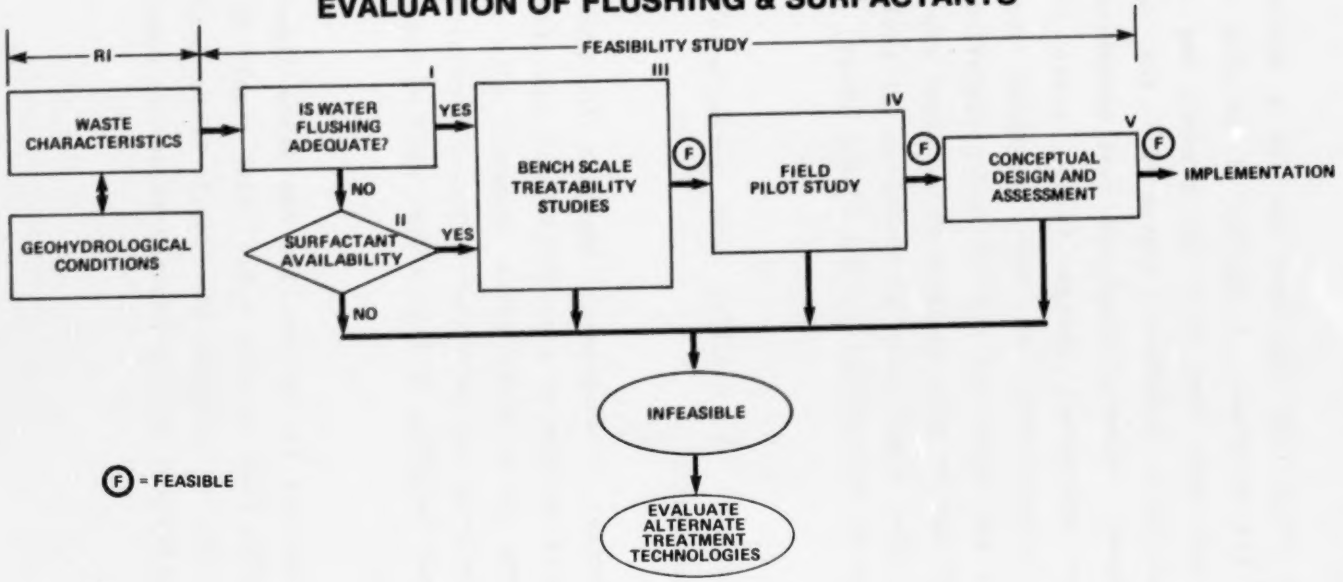
After the onsite pilot test has been run for a sufficiently long time to demonstrate that the microbes are capable of in situ biodegradation of the waste materials and that they will not produce any adverse environmental impacts, the full-scale treatment system for the waste deposit can be conceptually designed. Order-of-magnitude cost estimates should be performed according to the conceptual design (i.e., costs for detailed design, engineering and construction of the treatment system; operation and maintenance costs; and costs for culture and preparation of the microbes for storage, transport and in situ application). These costs should be compared with those of the other remediation alternatives (if any) to determine whether this method should be implemented (USEPA 1984a; USEPA, 1985; Repa and Kufs, 1985).

6.3.2 Evaluation of Flushing and Surfactants For Waste Deposit Stabilization

Figure 6-2 illustrates a systematic approach to identifying commercially available surfactants (single or a mixture) which can effectively mobilize the organic contaminants at a given waste disposal site for further in situ treatment or for recovery and subsequent surface treatment. As shown in this figure, this approach consists of five steps; each of these steps is described below.

The preliminary steps are to characterize the waste disposal site during the remedial investigation (see Section 6.2). With regard to surfactants, it is particularly important to measure the total ionic strength, hardness and concentration of polyvalent cations because these can reduce the effectiveness of a surfactant.

FIGURE 6-2
EVALUATION OF FLUSHING & SURFACTANTS


RI
FEASIBILITY STUDY
WASTE CHARACTERISTICS
GEOHYDROLOGICAL CONDITIONS
I
IS WATER FLUSHING ADEQUATE?
YES
NO
II
SURFACTANT AVAILABILITY
YES
NO
III
BENCH SCALE TREATABILITY STUDIES
F
IV
FIELD PILOT STUDY
F
V
CONCEPTUAL DESIGN AND ASSESSMENT
F
IMPLEMENTATION
INFEASIBLE
EVALUATE ALTERNATE TREATMENT TECHNOLOGIES
F = FEASIBLE

6.3.2.1 Flushing With Water or Surfactants (Step I)

If water can dissolve the wastes, it should always be used because of its safety, low cost and because it will not introduce a new chemical into the waste site. Based on the organics identified during the RI, Table 3-2 of Section 3 should be consulted to check the solubilities and octanol-water partition coefficients (K_{ow}) of these organics. If Table 3-2 does not contain the required data, supplemental literature surveys or laboratory tests should be conducted to determine the solubilities and K_{ow} of the identified organic waste materials. If their solubilities are greater than $5 \times 10^{-2}M$ and log K_{ow} values are less than 2, water can be used to flush and recover the organics. Otherwise, surfactants should be considered.

6.3.2.2 Identify Commercially Available Surfactants (Step II)

This step will be performed only when water alone cannot dissolve the organic wastes. Based on the physical, chemical and geohydrological conditions of the waste deposit and the site (determined during the RI), certain commercially available surfactants may be identified from Tables 3-1 and 3-5 of Section 3. The selection of a surfactant will be dependent upon its degradation rate, toxicity and effectiveness in the environment of the waste disposal site (see Section 3 for detailed discussion).

6.3.2.3 Bench Scale Treatability Studies of Potential Surfactants (Step III)

In this step, the potential surfactants selected from Step II are screened in a series of laboratory tests so that the most effective surfactant (single or a mixture) can be identified. An example of such studies is presented by Ellis et al. (1984). The tests may include, but not be limited to, the following:

- The interaction between the surfactants and the wastes - In these tests, the effectiveness of the surfactants are determined by the solubilities of the wastes in the surfactant solutions. The chemical characteristics of the surfactant solutions after contact with the wastes should also be checked for toxicity (i.e., the wastes may be made more available, and therefore more toxic, by emulsion/solubilization).

- The interaction between the surfactants and the soil - These tests should determine whether the surfactants lose their effectiveness because of adsorption to soil at the site.
- The interaction between the surfactants and the groundwater - These tests would evaluate the effects of groundwater chemistry on the effectiveness of the surfactants (i.e., the potential for precipitation, neutralization or complexing of the surfactant by naturally-occurring constituents of the groundwater).
- Biodegradation tests with native microbes - These tests would determine whether the surfactants are biodegraded by the native microbes at the waste site, and the degradation rates at various surfactant concentrations.

The most effective surfactant can be selected by comparing these test results. If the test results indicate that none of the tested surfactants are likely to be effective, alternative in situ treatment methods may have to be investigated.

Following the identification of potentially-useful surfactants, or the determination that water flushing alone should be sufficient, the effectiveness (i.e., organic waste removal/recovery rates) of either water or the selected surfactant should be tested under laboratory simulation conditions. These simulation tests can be simple column tests (Ellis et al., 1984) or specifically-designed microcosm tests which can better represent the waste site conditions. In these tests, the optimum range of water or surfactant concentrations and flow rates for recovering the wastes should be determined. In addition, the chemical characteristics of the recovered surfactant solutions and their potential toxicity should also be analyzed.

6.3.2.4 On-Site Pilot Test (Step IV)

In this step, a representative plot at the waste site should be selected for running a pilot test to confirm the results obtained from laboratory screening and simulation tests. In addition, the delivery/recovery system designed and implemented for this pilot test would provide design and operation guidance for the full scale treatment facility. The conducting of pilot-scale tests is discussed further in USEPA (1984a) and Repa and Kufs (1985). The potential delivery/recovery systems are discussed in Section 6.4.

6.3.2.5 Facility Design and Cost-Effectiveness Assessment (Step V)

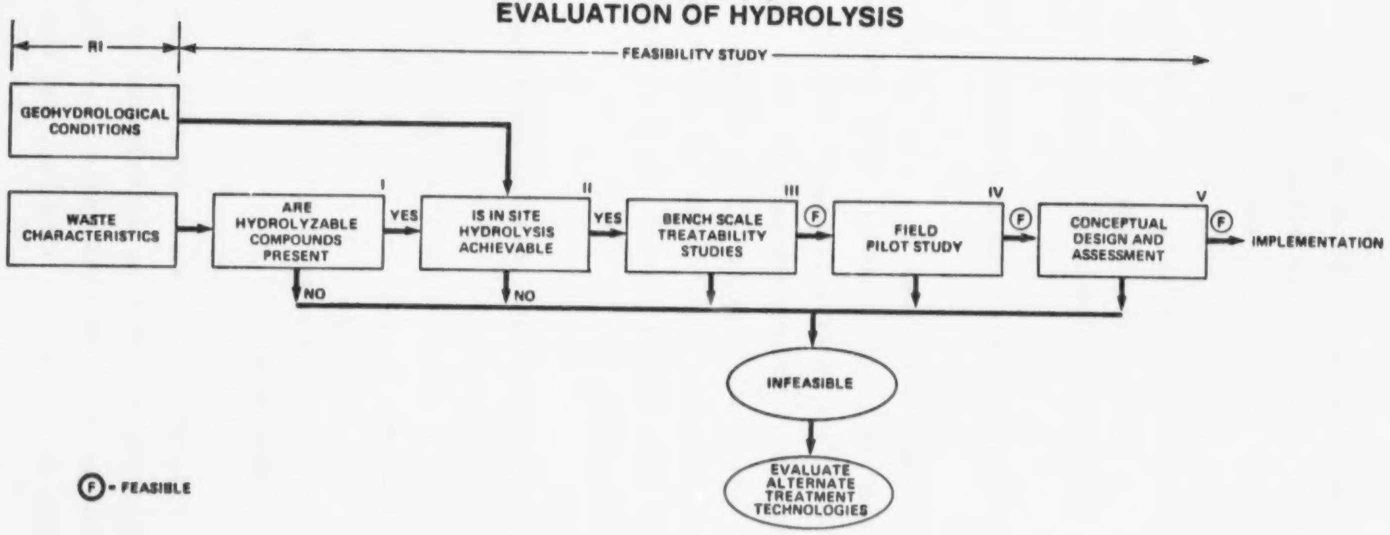
After the on-site test has shown that the water or selected surfactant is effective in recovering the wastes, and the surfactant (if used) is environmentally safe, the in-situ treatment facility for the waste site can be conceptually designed. Order-of-magnitude cost estimates should be made according to the conceptual design. These costs and the effectiveness of the system should be compared with those of other alternatives (if any) to determine whether this method should be implemented (USEPA, 1984a; USEPA, 1985; Repa and Kufs, 1985).

6.3.3 Evaluation of Hydrolysis for Waste Deposit Stabilization

Hydrolysis represents a major degradation process for many organic chemicals as reviewed in Section 4, and feasible in situ methods of accelerating hydrolysis rates are available. Thus hydrolysis is a potential in situ treatment method or mobilization method for waste deposits containing a variety of organic chemicals.

The application of hydrolysis to waste deposits will require implementation of a systematic evaluation approach as illustrated in Figure 6-3. This will be undertaken following the initial site investigation and contamination evaluation (RI, see Section 6.2). This approach includes:

FIGURE 6-3
EVALUATION OF HYDROLYSIS


RI
FEASIBILITY STUDY
GEOHYDROLOGICAL CONDITIONS
WASTE CHARACTERISTICS
I
ARE HYDROLYZABLE COMPOUNDS PRESENT
YES
NO
II
IS IN SITE HYDROLYSIS ACHIEVABLE
YES
NO
III
BENCH SCALE TREATABILITY STUDIES
F
IV
FIELD PILOT STUDY
F
V
CONCEPTUAL DESIGN AND ASSESSMENT
F
IMPLEMENTATION
INFEASIBLE
EVALUATE ALTERNATE TREATMENT TECHNOLOGIES
F - FEASIBLE

- Identifying the organic compounds in the waste susceptible to hydrolysis (Step I)
- Analyzing the effect of variables on hydrolysis rates and completeness, and assessing the need for and method of accelerating the hydrolysis rate (Step II)
- Bench scale treatability studies (Step III)
- Design and implementation of a field demonstration program (Step IV)
- Assessment of the field demonstration program and judging the feasibility of the hydrolysis system (Step V)

The procedures for assessing the potential application of hydrolysis are discussed below.

6.3.3.1 Identify Organic Compounds Susceptible to Hydrolysis (Step I)

Based on their hydrolysis half lives and potential for acceleration of hydrolysis, organic compounds can be divided into three general groups: a hydrolysis-resistant group, a hydrolysis-susceptible group (i.e., with catalysis or pH adjustment) and a hydrolyzable group. Tables 4-1, 4-2 and 4-11 summarize the types of chemical compounds that are generally resistant or susceptible to hydrolysis and Tables 4-3 through 4-10 present the hydrolysis half-lives for a variety of compounds. The application of hydrolysis is suitable for the hydrolyzable group, and may be possible for the hydrolysis-susceptible group. Organic compounds in the waste deposit are first identified by group. If the waste deposit contains both hydrolyzable and non-hydrolyzable compounds, more laboratory treatability testing and cost-effectiveness analysis may be required to confirm the feasibility of hydrolysis and the need for additional treatment of the non-hydrolyzable compounds.

6.3.3.2 Effects of Site Conditions on Hydrolysis and Potential for Acceleration of Hydrolysis Rates (Step II)

A hydrolyzable or hydrolysis-susceptible waste deposit may still be precluded from in situ treatment by hydrolysis due to the effects of pH, temperature, solvent composition, or difficulty of catalysis. The effect of pH on hydrolysis rate is pronounced in cases where acid- or base-catalyzed hydrolysis is important, changing the overall hydrolysis rate by up to one order of magnitude for one unit change in pH (see Figures 4-1 and 4-2). Tables 4-3 through 4-10 summarize the effects of pH on a variety of organic compounds.

Because the hydrolysis rate is a function of temperature, extrapolating laboratory temperature hydrolysis data to environmental conditions may represent a significant source of error. In general, a $10^{o}C$ ($18^{o}F$) decrease in temperature produces a 2.5 times decrease in the hydrolysis rate. Hydrolysis rates are also affected by solvent composition, i.e., ionic strength. Increasing the ionic strength can either accelerate or retard hydrolysis. Catalysis or retardation of hydrolysis by surfactants can also significantly alter hydrolysis rates (N Wolfe, USEPA, Athens, GA: personal communication). Each of these factors must be evaluated for the hydrolyzable compounds present to determine whether their hydrolysis rates may be unavoidably retarded by in situ conditions, or may be accelerated by altering these conditions.

Three types of hydrolysis processes, base-catalyzed, neutral and acid-catalyzed hydrolysis, may contribute to or affect the overall hydrolysis rates of organic chemicals in the environment. Base-catalysis of hydrolysis appears to be the most promising approach. The chemical classes potentially treated through acceleration of degradation by base-catalyzed hydrolysis are described in detail in Section 4 and presented in Table 4-11. The primary design concern for implementation of base-catalyzed hydrolysis in a waste deposit will be the production and maintenance of high pH (pH 9 to 11) conditions with saturation or high moisture content in the waste deposit.

6.3.3.3 Bench Scale Treatability Studies and Field Pilot Study (Steps III and IV)

Bench scale treatability studies and field pilot tests using site specific soil/waste matrices should be conducted prior to full scale implementation of hydrolysis treatment systems for waste deposits (USEPA, 1984a). The exact requirements for base addition in hydrolysis acceleration and the effects of pH alteration should be determined by laboratory tests. Acidic or highly buffered deposits or soils will require greater additions of base than poorly buffered, neutral or alkaline deposits. However, anionic and amphoteric (capable of acting as either an acid or base) species may be mobilized, and the sorption of organic species in the deposit may be affected by a significant change in the pH of the waste deposit matrix.

6.3.3.4 Cost-Effectiveness Assessment and Conceptual Design (Step V)

The laboratory and field tests will indicate the susceptibility to hydrolysis of the wastes, in situ hydrolysis rates and the potential for catalytic acceleration. In addition, the potential effects of site geohydrologic conditions (soil organics, groundwater chemistry) and side reaction products (which may be toxic) can be evaluated. These variables must be evaluated to determine the feasibility, environmental acceptability (risk assessment), and effectiveness of in situ hydrolysis of the waste deposit. The facility is conceptually designed and order-of-magnitude cost estimates are made so that a cost and effectiveness analysis can be performed (USEPA, 1984a; USEPA, 1985; Repa and Kufs, 1985).

It must be noted that at the present time, only limited investigations of hydrolysis in soils have been conducted. There is no practical field experience for the control of hydrolysis rates in waste deposits. However, conditions favorable to base-catalyzed hydrolysis can be produced using available equipment and reagents. That is, lime can be applied to the surface and irrigated to produce the base catalysis; alternatively NaOH solution can be used. Again, the selection of pH-controlling reagents will be based on the results of bench scale treatability studies.

6.3.4 Evaluation of Oxidation for Waste Deposit Stabilization

The potential application of three oxidants (ozone, hydrogen peroxide, and hypochlorites) to waste deposits is evaluated in Section 5. While these oxidants are reactive with a wide variety of organic compounds and have demonstrated applications in wastewater treatment, significant potential problems may preclude their use as in situ treatment agents for waste deposits.

Hydrogen peroxide is a weaker oxidizing agent than ozone, but its stability in water is considerably greater. However, the decomposition of hydrogen peroxide to oxygen may be catalyzed by iron or certain other metals; therefore effective delivery of hydrogen peroxide throughout an entire waste deposit may be difficult or impossible because of the relatively low transport velocities achievable in waste deposits compared to accelerated in situ decomposition rates. Prior to consideration of hydrogen peroxide as an in situ treatment method, it will be necessary to investigate the stability (or rate of decomposition) of hydrogen peroxide in a specific waste deposit matrix, as well as its effectiveness in treating contaminants of concern. In the event that hydrogen peroxide is not determined to be effective as a treatment agent, it may find usage as a source of oxygen in a waste deposit to support aerobic microbial degradation of the wastes (Wetzel et al., 1985).

If the effectiveness of hydrogen peroxide as an oxidizing agent for a waste treatment can be demonstrated, its application to a waste deposit does not appear to present significant problems with respect to equipment selection. The approach described for the evaluation of hydrolysis (Section 6.3.3, except for the determination of catalyst-accelerated hydrolysis) is directly applicable to the evaluation of the feasibility of using hydrogen peroxide. Hydrogen peroxide is available commercially in a variety of concentrations and freely dissolves in water at all concentrations. At low concentrations hydrogen peroxide solutions have densities and viscosities similar to water. The potential hazard of violent reactions of certain organic materials with hydrogen peroxide should, however, be recognized. Applications of dilute solutions may be necessary to avoid possible explosive hazards. Since addition of very dilute hydrogen peroxide solutions to a waste deposit could result in flushing of contaminants, recovery methods as well as delivery methods should be included in system design.

Potential application of ozone to organic contaminants in waste deposits is discussed in Section 5.2. While ozone is an effective oxidizing agent for many organic compounds in wastewater treatment applications, its relatively low stability in aqueous systems, particularly in the presence of certain chemical contaminants, may preclude its effective application to waste deposits. As indicated in Section 5.2, the half-life of ozone in natural waters is less than one-half hour. Considering that flow rates of water through waste deposits are likely to be on the order of inches/hour or less, it is unlikely that effective oxidant doses of ozone can be delivered outside of the immediate vicinity of the point of application (i.e., within inches or feet of an injection point). For this reason, design of a feasible application system for in situ treatment by ozone is unlikely. However, ozone may be used to provide an oxygen source for biodegradation (see Section 5.2, and Nagel, 1982).

Demonstrations of the effectiveness of hypochlorite as an oxidizing agent for organic materials are extremely limited (Section 5.3). In addition, hypochlorite reacts with organic compounds as a chlorinating agent as well as an oxidizing agent, and there is a significant chance that hypochlorite additions to waste deposits may lead to production of undesirable chlorinated by-products (e.g., chloroform) rather than oxidative degradation of the wastes. Therefore, the usage of hypochlorite is not recommended.

6.4 Application and Design of Delivery/Recovery Systems for In-Situ Treatment

The successful application of chemical solutions to a hazardous waste deposit for in situ treatment or mobilization of contaminants from the deposit requires the selection of a technically sound and cost effective delivery/recovery system. A systematic approach for site evaluation, treatment method selection and conceptual process design is required prior to final facility design. Prior to the implementation of a delivery/recovery system, a laboratory test program and a field demonstration program would be required as needed to fill data voids.

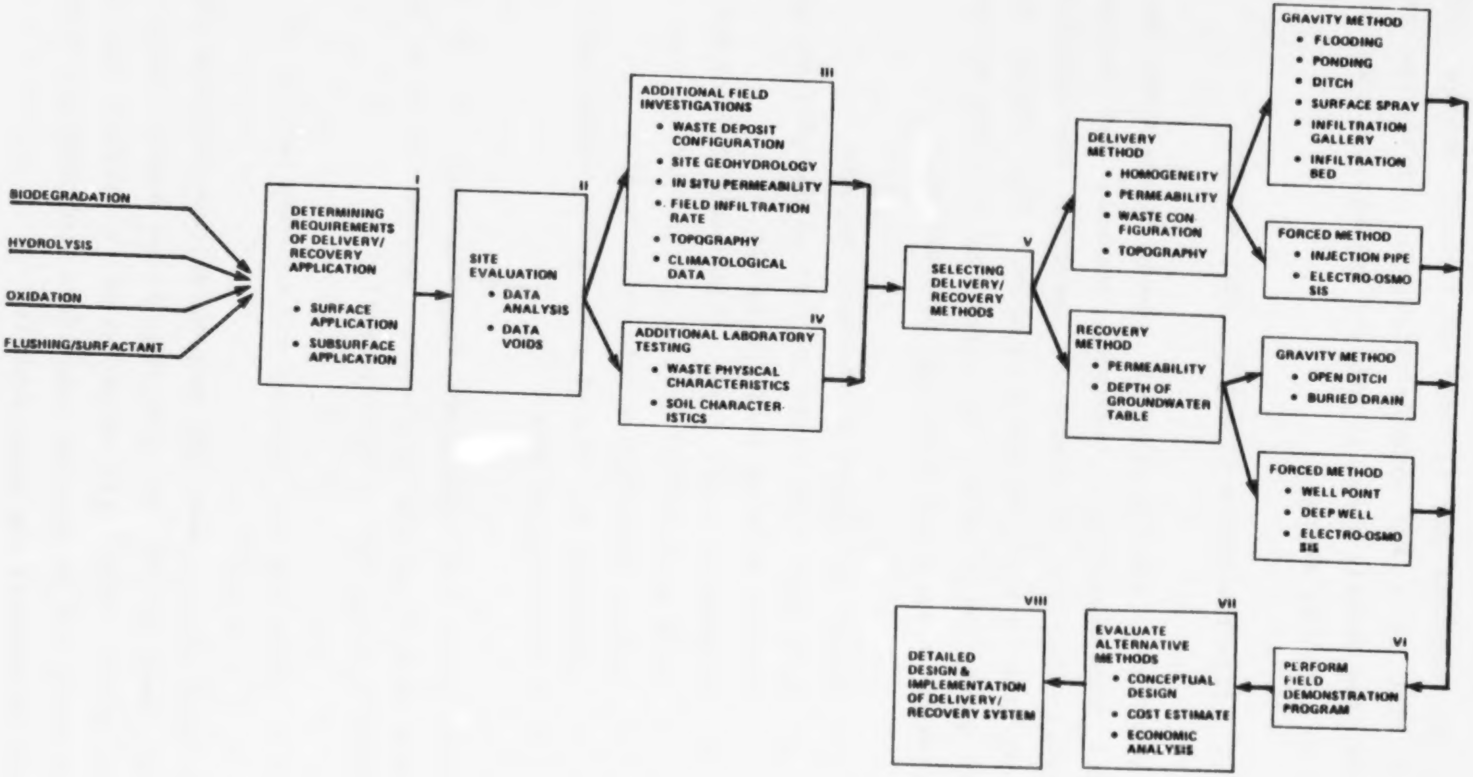
The treatment techniques and the site parameters that govern the design and performance of the delivery/recovery technologies were discussed in Section 1. Based on these discussions, a matrix of decision factors consisting of relevant technical criteria was developed in order to guide in the conceptual design of feasible delivery and recovery systems for a given set of site conditions (Tables 1-5 and 1-6). The systematic approach for implementing a delivery/recovery system as shown in Figure 6-4 consists of site evaluation, a program of additional field and laboratory testing (as required), identification of alternative methods for delivery and recovery of solutions, conceptual design of the alternative remedial technologies, economic evaluation, system selection and finally detailed design and implementation of the delivery/recovery system.

6.4.1 Determining the Requirements of a Delivery/Recovery System (Step I)

Analysis of the chemicals present in and the characteristics of the waste deposit would lead to the selection of the treatment methods to be used. Biological agents, chemical hydrolysis, oxidation or flushing methods using water or surfactants would be selected as described in Section 6.3 before the specific delivery/recovery sytstem is identified. This determination would define the processes required to deliver the treatment agents and possibly also dictate the recovery methods.

There are many alternative methods for combining the reagent with a delivery system. For example in situ oxidation might require forced injection of hydrogen peroxide directly into the waste because of its reactivity with soil. Alternatively, flushing with water into the same deposit could rely upon passive, gravity type delivery systems since there is no degradation of the reagent (water) during its time of passage through the soil medium to the

FIGURE 6-4
SYSTEMATIC APPROACH TO DELIVERY/RECOVERY SYSTEM SELECTION


BIODEGRADATION
HYDROLYSIS
OXIDATION
FLUSHING/SURFACTANT
I
DETERMINING REQUIREMENTS OF DELIVERY/ RECOVERY APPLICATION
• SURFACE APPLICATION
• SUBSURFACE APPLICATION
II
SITE EVALUATION
• DATA ANALYSIS
• DATA VOIDS
III
ADDITIONAL FIELD INVESTIGATIONS
• WASTE DEPOSIT CONFIGURATION
• SITE GEOHYDROLOGY
• IN SITU PERMEABILITY
• FIELD INFILTRATION RATE
• TOPOGRAPHY
• CLIMATOLOGICAL DATA
IV
ADDITIONAL LABORATORY TESTING
• WASTE PHYSICAL CHARACTERISTICS
• SOIL CHARACTERISTICS
V
SELECTING DELIVERY/ RECOVERY METHODS
DELIVERY METHOD
• HOMOGENEITY
• PERMEABILITY
• WASTE CONFIGURATION
• TOPOGRAPHY
RECOVERY METHOD
• PERMEABILITY
• DEPTH OF GROUNDWATER TABLE
GRAVITY METHOD
• FLOODING
• PONDING
• DITCH
• SURFACE SPRAY
• INFILTRATION GALLERY
• INFILTRATION BED
FORCED METHOD
• INJECTION PIPE
• ELECTRO-OSMOSIS
GRAVITY METHOD
• OPEN DITCH
• BURIED DRAIN
FORCED METHOD
• WELL POINT
• DEEP WELL
• ELECTRO-OSMOSIS
VI
PERFORM FIELD DEMONSTRATION PROGRAM
VII
EVALUATE ALTERNATIVE METHODS
• CONCEPTUAL DESIGN
• COST ESTIMATE
• ECONOMIC ANALYSIS
VIII
DETAILED DESIGN & IMPLEMENTATION OF DELIVERY/ RECOVERY SYSTEM

deposit. It is difficult to generalize as to how the treatment per se becomes a factor in selecting the delivery or recovery system. In some cases the treatment will be a key consideration; in others the site geohydrologic conditions, the deposit location and the anticipated costs will influence the decision to a greater degree.

6.4.2 Site Evaluation (Steps II, III, and IV)

Characterization of the contaminants present in the waste deposit is necessary to select the appropriate treatment methods, and determination of site geohydrologic features is needed to establish the location, selection and design of the delivery/recovery system. The field investigation data generated during the RI should be reviewed to identify any data voids. The RI should provide at least the following information:

- Extent and nature of the waste deposit
- Site soil characteristics such as porosity and permeability
- Surface drainage characteristics
- Groundwater table depth, groundwater flow direction and velocity
- Field permeability testing of the waste deposit and host materials
- Surface infiltration rate determination
- Laboratory analysis of soil, waste deposit and groundwater samples
- Climatological data.

Additional field and laboratory investigations may be required for the evaluation of certain delivery/recovery methods if it is determined that the data provided in the RI are insufficient.

6.4.3 Selecting the Delivery and Recovery Methods (Steps V)

The selection of the most appropriate delivery/recovery methods and systems would be based on the configuration of the waste deposit (areal extent and vertical depth), hydrologic characteristics (surface and subsurface) of the waste deposit, and surface and subsurface geohydrologic characteristics of the materials surrounding the waste deposit.

6.4.3.1 Delivery Methods

The matrix for selection of delivery methods is presented in Table 1-5. This table illustrates that forced delivery methods are applicable for all conditions. The choice of a gravity delivery method is more dependent on the listed parameters. The design factors for the delivery methods and their associated design criteria are discussed below.

Location of the Deposit in Relation to Existing Groundwater Table --

As may be seen from Table 1-5, if the waste deposit is located in the unsaturated zone all of the gravity and forced delivery systems may be applicable. Presence of the waste deposit in the saturated zone eliminates virtually all of the gravity delivery methods (with the possible exception of ponding). Forced delivery appears to be the most effective delivery method for waste deposits located in the saturated zone.

Contamination Present at the Surface --

This consideration may eliminate certain gravity based delivery systems (such as the use of ditches, infiltration galleries and infiltration beds) which require excavation to construct and therefore cannot deliver solution to the surface. In this case, gravity based delivery systems applied at the surface (i.e., flooding, ponding and surface spraying) could be applicable. Injection into a waste deposit via forced injection can treat waste below the surface but it would need to be supplemented by a gravity method to assure complete treatment of surficial as well as deeper waste materials.

Waste Deposit Covered by an Impermeable Layer --

This parameter has no bearing for the forced delivery methods, but it will have a significant impact for gravity delivery methods. For example, flooding and spraying cannot be utilized as delivery methods if the deposit is separated from the surface by an impermeable layer of soil or is covered by an impermeable synthetic material.

Topography --

Topographic considerations will limit, in part, the extent of applicability of gravity flow methods. For example, flooding or ponding delivery methods cannot be utilized on a steep slope although trenches may be feasible. However, topography will not affect the forced delivery methods.

Infiltration Rate --

The infiltration rate governs the application rate of reactant on the top layer of the deposit or soil. It has no bearing in the selection of forced methods. In surface gravity applications this will play a major role, and may eliminate flooding, surface spraying, ponding or ditching as potential delivery methods.

Hydraulic Conductivity of the Waste Deposit and Surrounding Soil --

The hydraulic conductivity of the soil and waste deposit will dictate the flow characteristics within and around the deposit. If the hydraulic conductivity of the deposit is high and is equal to or greater than that of the surrounding soil, low net pressure and short time durations would be required for a solution to pass through the deposit. In this case, gravity delivery systems may be used. Low hydraulic conductivity of the waste deposit indicates that the deposit will not be easily drainable and will require higher pressure and longer times for a solution to move through the deposit. If the waste deposit has a lower hydraulic conductivity than the surrounding soils, solutions delivered by gravity methods would bypass the deposit. In either case, a forced delivery system would be required.

Gravity delivery methods would be applicable if the waste deposit and surrounding medium have hydraulic conductivities in the range of 1×10^{-1} cm/sec to 1×10^{-3} cm/sec (280 to 2.8 ft/day). Forced delivery methods would be required for a waste deposit or soils with a hydraulic conductivity between 1 x 10^{-3} cm/sec and 1 x 10^{-4} cm/sec (2.8 to 0.28 ft/day). For a hydraulic conductivity less than 1 x 10^{-4} cm/sec (0.28 ft/day), forced injection assisted by electro-osmosis used as a recovery method may be the only effective system.

Depth to Bottom of the Waste Deposit --

The cutoff for this parameter was chosen based on engineering judgement. If the depth to the base of the deposit is too great it may take too long for a solution to travel through the deposit under the force of gravity. Based on this condition, a reasonable cut-off point for gravity delivery methods was chosen at 5 meters (16 feet).

In addition to the parameters and conditions presented in Table 1-5, the homogeneity of the waste deposit and surrounding soil media is important, although very difficult to quantify. Waste deposits and soils with large variations in hydraulic conductivity as a function of depth or lateral location vastly complicate the delivery of treatment reagents. Gravity methods are much more effective in relatively homogeneous deposit and soil environments where the applied solution can be evenly distributed throughout the deposit. In a heterogeneous environment, the waste deposit probably cannot be effectively treated by gravity delivery methods. Only forced delivery methods offer any promise in such cases.

In general, gravity delivery methods are effective when the waste deposit is situated in an unsaturated zone at the surface or with a shallow, relatively permeable overburden, and the depth to bottom of the deposit is limited to 5 meters (16 feet) with hydraulic conductivity greater than 1 x 10^{-3} cm/sec (2.8 ft/day). Forced delivery methods will be most effective for waste deposits covered by thick overburdens of significant depth (more than 5 meters). A forced method utilizing electro-osmosis could be considered for solution injection into a deposit with hydraulic conductivities lower than 1 x 10^{-4} cm/sec, although at present the applicability and effectiveness of electro-osmosis has not been demonstrated. In general, forced methods should be highly effective for waste deposits with hydraulic conductivities in the range of 1 x 10^{-1} cm/sec to 10^{-4} cm/sec (280 to 0.28 ft/day).

6.4.3.2 Recovery Methods

Table 1-6 indicates the applicability of various recovery methods for different site characteristics. Two parameters, depth to the recovery zone and hydraulic conductivity, are considered sufficiently important to include in the matrix. Although additional parameters (such as effective porosity and storativity) may play an important role in designing deep well or well point systems, these two parameters are the most appropriate guide for the preliminary selection of recovery methods. It should be noted that the recovery of injected solutions will be from the saturated zone (water table aquifer) and normally the recovery method(s) will be installed beyond the boundary of the waste deposit. The depth to the recovery zone is chosen as a prescriptive parameter because gravity methods are generally impractical beyond a 5 meter (16 foot) depth. The hydraulic conductivity will dictate the drainage characteristics and thereby control the selection of recovery (dewatering) methods.

The following design criteria, condensed from the matrix of criteria for selecting a recovery system (Table 1-6), could be used as a basis for conceptual design:

1. Gravity recovery systems (open ditches and buried drains) or forced recovery systems (well points or deep wells) are applicable for a site having a hydraulic conductivity between 1 x 10^{-1} cm/sec and 1 x 10^{-3} cm/sec (280 to 2.8 ft/day). A vacuum well point system or possibly a deep well system would be suitable for a site with a hydraulic conductivity in the range of 1 x 10^{-3} cm/sec to 1 x 10^{-4} cm/sec (2.8 to 0.28 ft/day). The electro-osmosis method may be considered for low permeability conditions (below 1 x 10^{-4} cm/sec or 0.28 ft/day), but considerable experimentation and laboratory simulation and testing would be a necessary precursor to use of this method.

2. A multi-stage well point or vacuum well point system would be required for a depth between 5 meters and 12 meters (16 feet to 40 feet).

3. Open ditches and buried drains should be limited to depths of less than 5 meters (16 feet) and must be within the zone of saturation. Deep wells would be practical for a depth of more than 5 to 12 meters (16 to 40 feet).

In general, gravity recovery methods are suitable for a shallow recovery zone (depth to water table from the surface should not be more than 5 meters). For a deeper recovery zone, forced recovery methods must be employed.

6.4.4 Field Demonstration Program (Step VI)

A site specific field demonstration program for the selected feasible methods is undertaken if necessary to evaluate the effectiveness of the methods and to generate design information such as ditch spacing or well spacing which will be required for proper delivery and recovery of the treatment agent.

6.4.5 Evaluating Alternative Methods (Step VII)

Based on the field demonstration program, alternative delivery/recovery systems are developed and a conceptual design and associated cost evaluation is performed. Based on the cost analysis and treatment system effectiveness, final selection of a delivery/recovery system is made for subsequent implementation (USEPA, 1984a; USEPA, 1985; Repa and Kufs, 1985).

6.4.6 Detailed Design and Implementation (Step VIII)

The final steps of engineering and design for installation of an in situ treatment system would be the detailed design, specification preparation, equipment procurement and installation of the following facilities necessary to apply, distribute and collect treatment solutions:

- Treatment agent storage, preparation and delivery facilities and equipment,
- Earthwork for site preparation,
- Delivery and recovery system facilities and equipment, and
- Monitoring system facilities and equipment.

A number of recent publications give a comprehensive description of how in situ treatment methodologies can be evaluated, tested and undertaken, and reflect the general principles outlined in this report. These studies include Jhaveri and Mazzacca (1983), USEPA (1984b), Ryckman (1984), Wetzel et al. (1985), Flathman et al. (1983), Flathman et al. (1984), and Flathman and Caplan (1985). Most of these studies, which present detailed case histories of in situ treatment by biodegradation or hydrolysis (Ryckman, 1984), have been described in previous sections of this report.

6.5 Case History of RI/FS and In Situ Treatment of Contaminated Soil and Groundwater

6.5.1 Site Summary

In August 1975 contamination was observed in a small creek that discharges into Allendale Brook in the Town of Waldwick, NJ. Biocraft Laboratories, a small synthetic penicillin manufacturer is located on a 1.72 ha (4.3 acre) plot near the contaminated creek within an industrial park in Waldwick. It was determined that leakage had ocurred in underground tanks used to store waste solvent between 1972, when the plant commenced operation, and 1975, when the contamination was discovered, (Jhaveri and Mazzacca, 1983; USEPA, 1984c). The waste solvents seeped into an adjacent storm sewer and thence drained into the stream, where a fish kill in 1973 was attributed to the contamination. The local shallow aquifer was contaminated and it was feared that a town drinking water well was threatened by the plume. It is estimated (Jhaveri and Mazzacca, 1983) that the following contaminants probably leaked into the subsurface environment:

methylene chloride	82310 kg	(181500 lbs)
n-butyl alcohol	30305 kg	(66825 lbs)
dimethyl aniline	11925 kg	(26300 lbs)
acetone	4840 kg	(10890 lbs)

6.5.2 Remedial Investigation

The Biocraft site was well characterized both geohydrologically and chemically. Figure 2-1 (in Section 2) is a site plan for the Biocraft site showing the approximate configuration of the contaminant plume prior to remediation. Figure 6-5 is the configuration of the water table at the site before implementation of remediation. Six groundwater monitoring wells were installed at the site in January 1976, followed by 22 more wells in June 1976. These were used both to monitor and selectively pump contaminated water. The basic results of the monitoring and testing program were that:

1) The contaminant plume (as measured by COD greater than 100 mg/liter) roughly followed the plume outline show in in Figure 2-1 and was approximately 0.71 ha (1.75 acres) in area. It was estimated that 9175 m^3 (12000 yd^3) of soil were contaminated.

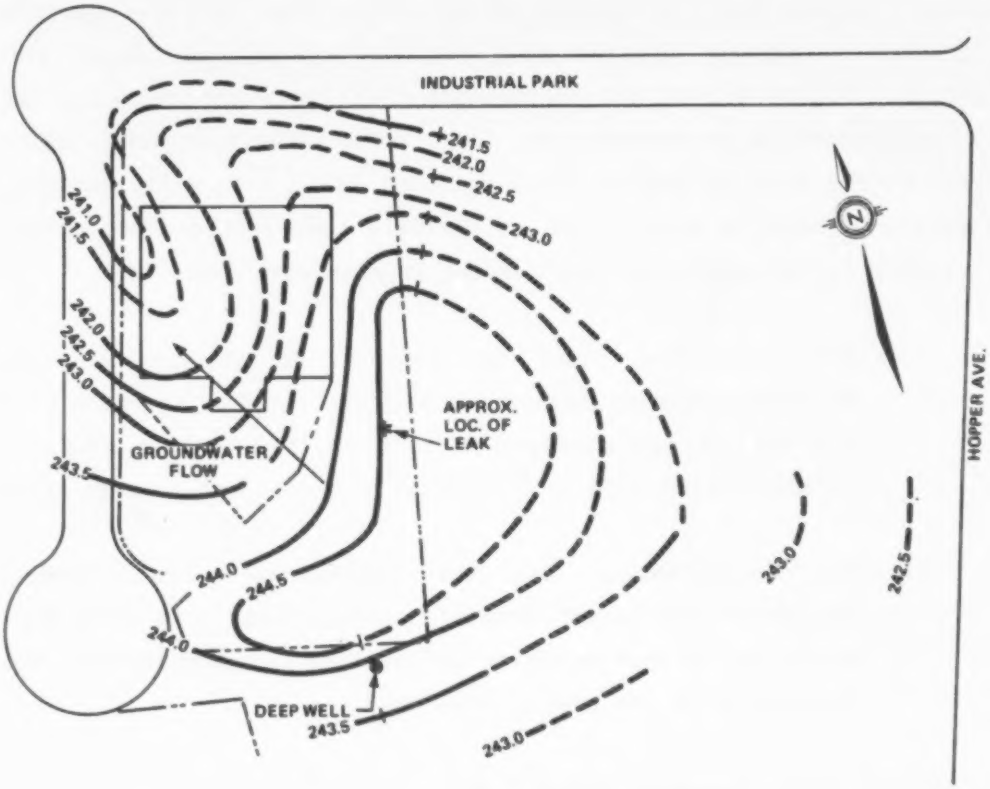
2) The contamination had not penetrated a semi-consolidated silt/fine sand layer located approximately 4 m (12 ft) below grade and no contamination had entered the deep aquifer which is the source of the town's water supply.

The tabulation below presents chemical data taken from the six sampling wells at the site during Jan - June 1976.

Parameter	Concentration Range
pH	5.2 - 7.5
BOD	2 - 21000 mg/l
COD	8 - 31000 mg/l
TOC	2 - 9625 mg/l
Cl^-	5 - 6246 mg/l

FIGURE 6-5

GROUNDWATER SURFACE CONTOURS BIOCRAFT SITE


INDUSTRIAL PARK
241.5
242.0
242.5
243.0
241.0
241.5
242.0
242.5
243.0
243.5
GROUNDWATER FLOW
APPROX. LOC. OF LEAK
244.0
244.5
244.0
DEEP WELL
243.5
243.0
243.0
242.5
HOPPER AVE.
N

(SOURCE: JHAVERI AND MAZZACCA, 1983)

An onsite test well sampled in 1981 (just before the biodegradation operation began at the site) revealed groundwater concentrations of 85 mg/l acetone, 55 mg/l methylene chloride and 648 mg/l COD (USEPA, 1984c).

The site is located in an area of unstratified and stratified glacial drift. A layer of silt and gravel approximately 3 ft thick is found at the surface and is underlain by glacial till to a thickness of 8 to 15 feet. Based on slug tests at 5 on-site wells, the hydraulic conductivity of the glacial till layer ranges from 1.7×10^{-3} to 9.4×10^{-7} cm/sec (0.02 to 36 gallons/day per ft^2). Approximately 12 m (40 feet) of semi-consolidated silt and fine sand underlies the till layer. This layer, which lies at an average depth of about 4 m (12 ft) below grade, is considered to be an aquiclude.

For further detail the reader is referred to USEPA (1984c) and Jhaveri and Mazzacca (1983) for a complete description of the extent of contamination at the site, site characteristics (soil properties, aquifer conditions), the monitoring program and the reactions and depositions of state and local regulatory bodies and interested parties.

6.5.3 Feasibility Study

The evaluative process leading to the selection of biodegradation as compared with other technologies (e.g., slurry walls, excavation) described in USEPA (1984c). This section describes the methodology followed by Biocraft Laboratories in technically developing the biodegradation system for their site.

Biocraft and their subsidiary Groundwater Decontamination Systems (GDS), which holds a patent on the system ultimately installed at the site, required approximately 2-1/2 years to proceed through the research and development stage of the biodegradation system, that is to proceed through Steps II through VII as presented on Figure 6-1.

Biocraft and its consultants selected and developed the biodegradation alternative in May 1979. The alternative included four elements:

1) Collection of the contaminated plume in a downgradient buried trench,

2) Surface treatment of the collected groundwater in a bioreactor to remove contamination and aerate the water,

3) Reintroduction of the treated water upgradient via infiltration trenches in order to flush the soil and to supplement the subsurface microbe population, and

4) Promotion of subsurface biological activity through the use of aeration wells.

Establishment of biodegradation as an in situ treatment technology was faciliated by:

1) The relatively homogeneous nature of the well-characterized contaminant plume,

2) The presence of soil contamination within the saturated portion of the surficial aquifer (i.e., above the aquiclude),

3) The permeability of the soils which lay within the feasible range for carrying out in situ treatment, and

4) The depth to the deposit (or plume) was less than 5 meters (16 ft).

These conditions indicate that gravity delivery and recovery systems would be suitable for the site (see Sections 1.2 and 1.3 of this report).

When Biocraft started the investigation in July 1978 the biodegradability of methylene chloride, the principal pollutant at the site, was not clearly known (Jhaveri and Mazzacca, 1983). To determine whether readily available microbes would be capable of degrading methylene chloride (i.e., to perform Step II), contaminated groundwater was inoculated with soil samples taken from the

Biocraft site itself as well as uncontaminated (control) samples from the homes of various employees. Completion of this step indicated that the onsite soil sample held the most promising microbial population.

The research effort then turned to the identification of limiting factors, i.e., Step III of Figure 6-1. A shaker flask study using contaminated water as the carbon source was undertaken to determine optimum growth conditions. Jhaveri and Mazzacca (1983) provide details on nutrient media tested and USEPA (1984c) provides a tabulation of the experimental results. The conclusions of this step were:

1) Nitrogen and phosphorus addition increased cell growth,

2) Phosphorus addition (as dibasic phosphate) supplied buffering capacity to the medium thus accounting for HCl formation associated with methylene chloride degradation, and

3) Anaerobic study results were not favorable.

Having established that the onsite microorganisms were effective in degrading methylene chloride, Biocraft/GDS proceeded to bench scale treatability and field pilot studies (i.e., Steps VI and VII). The basic elements of this portion of the program consisted of:

1) Aeration and nutrient addition to an onsite well. This test demonstrated the feasibility of subsurface aerobic activity: a 100 fold increase in cell count was observed after 7 days

2) Bench scale batch testing in fermentors. Various temperatures and aeration rates were tested.

3) Bench scale continuous testing in fermentors. These tests established the percent destruction of methylene chloride as a function of the retention time, and

4) Pilot plant studies conducted in two 208 liter (55 gallon) drum reactors. Air sparging, temperature control systems, and nutrient feed methods were tested. The process retention time, nutrient feed rate and aeration rate were established.

The pilot plant showed that methylene chloride could be reduced by 99% of its inlet concentration, butanol levels could be reduced by 96% and dimethyl aniline concentrations could be reduced by 59%. More detailed data and process difficulties are reported upon in USEPA (1984c) and Jhaveri and Mazzacca (1983). Biocraft/GDS were sufficiently satisfied with results of this series of studies to proceed to the development of a full scale reactor which is described briefly below and in detail in both of the above references.

In summary, performance by Biocraft/GDS of Steps I-VIII as shown in Figure 6-1 established the feasibility of both an above ground reactor using onsite microorganisms and of bringing about subsurface biological degradation. The following subsection compares the site and waste characteristics at the Biocraft site to the guidance presented in Section 1 of this report on the selection of delivery and recovery systems and describes the entire treatment system at the site.

6.5.4 Description of the Treatment System

The shallow groundwater table (0-3 meters below the surface) and depth to the aquiclude of less than 5 meters (16 ft), combined with soil permeabilities in the range of 1×10^{-3} cm/sec, indicated that a gravity delivery and recovery system could be considered (see Section 1.5 of this report for a discussion of parameters used in selection of delivery/recovery systems). As shown in Figure 6-5, although a groundwater mound exists in the southeast corner of the site, groundwater flow is generally to the northwest. Based on these considerations, Biocraft and its consultants designed the recirculating in situ and above ground (bioreactor) treatment system illustrated in Figure 2-2. The operation of this system would provide both plume containment and removal of the source. This system is relatively passive and unobtrusive: The delivery and recovery systems are below ground and invisible to passersby, and implementation of the system did not require disruption of the Biocraft operation, which other actions such as excavation would clearly have done.

The delivery system consists of two "recharge trenches" (infiltration galleries), one of which is illustrated in cross-section in Figure 2-2. The trenches are approximately 30 m long, 1 m wide and 3 m deep, and were excavated by backhoe (USEPA, 1984c). The trenches are lined on all sides but the front (Figure 2-2) with a 15 mil plastic liner to direct the injection water toward the waste deposit. The trenches are filled with 5 cm diameter washed stone to the surface (Figure 2-2). A 5 cm slotted pipe placed along the trench (1.5 m from the bottom) delivers recharge water at a rate of about 25,900 l/day (6850 gallons/day) per trench. Each trench also has two monitoring wells (one at each end) which can also be used to flush the trenches if sludge accumulates.

The recovery system, located approximately 90m (300 ft) northwest of the infiltration trenches, consists of a buried trench and slotted pipe collection system (Figure 2-2). The trench is about 24 m long, 1.2 m wide and 3 m deep, and is filled with a layered, washed stone gravel pack (USEPA, 1984c). Groundwater is pumped at a rate of 38 l (10 gallons) per minute from a slotted central collection well which is also fed by the collection pipes. Groundwater is also pumped from two bucket wells at the southern edge of the site to intercept the southerly component of groundwater flow from the groundwater mound (USEPA, 1984c; Jhaveri and Mazzacca, 1983).

The in situ aeration system (Figure 2-2) consists of nine aeration wells, spaced about 9 m away from each other and arranged in a rectangular matrix 9 m wide and 30 m long (USEPA, 1984c). This arrangement was based on the assumption of a 4.5 m radius of influence of each aeration point. Air is continuously injected at a pressure of 28-62 kN/m^2 (4-9 psi).

The surface treatment system (bioreactor) consists of a dual system of two aeration and two sludge settling tanks, each tank having a capacity of 20,000 l (5400 gallons). The stainless steel, temperature-controlled tanks were originally used for milk transport. Influent water from the collection trench and two interceptor wells is pumped first to the aeration tanks, where most of the biodegradation occurs (Jhaveri and Mazzacca, 1983). Air is added to each tank through a series of porous ceramic tube diffusers at a rate of 0.8 m^3 per minute. Temperature is kept constant at 20°C (68°F) using a single pass steam coil installed in the tanks. A nutrient solution is metered into the aeration tanks as required. Effluent air from the aeration tanks is passed through replaceable activated carbon adsorbers to remove any volatilized organics.

The effluent stream from the aeration tanks is combined and pumped to the sludge settling tanks in which some biomass solids are settled out and recycled to the aeration tanks. The supernatant from the settling tanks is pumped to the reinjection trenches. An important point is that much of the biomass is allowed to pass with the supernatant into the recharge trenches in order to continually inoculate the trench and subsurface with microorganisms. Waste sludge production is approximately 42 l (11 gallons) per month.

The system is presently operating at an average flow rate of 36 l (9.5 gallons) per minute with a retention time in the aeration tank of 17.5 hours. The system has the capability to handle a flow of up to 53 l (14 gallons) per minute or 76,000 l (20,000 gallons) per day with a retention time of 12 hours (Jhaveri and Mazzacca, 1983).

Biocraft personnel indicate that approximately 60% of the total biodegradation of the contaminants takes place in the surface reactors, and approximately 40% takes place in situ (i.e., in the soil and groundwater) (Dr V Jhaveri, personal communication, 1985). The average one-cycle removal efficiency for the surface bioreactors is 88-98% for all contaminants except dimethyl aniline (which is 64%) (Jhaveri and Mazzacca, 1983). The system began operation in August, 1981. As of June 1985, Biocraft personnel report that the site is 95% remediated, and operation is expected to be terminated in 1986.

6.5.5 Cost Data for the Biocraft Site

The following information is presented to illustrate the cost of applying in situ treatment using biodegradation. Although the Biocraft site data may not be directly extrapolated to other sites of differing extent or differing contaminant inventories, certain conclusions may be drawn from these data which illustrate the decisions which have to be made, during the evaluation of in situ treatment systems.

Table 6-2 presents data on the cost of remedial action at the Biocraft Site. The data are taken from USEPA (1984c) and from personal communications with personnel at the Biocraft Site. The total capital cost for the remediation (sum of Items 1, 2 and 3 in Table 6-2) was $925,678 of which $446,280 (about 48%) was expended during the feasibility portion of the remediation. Further, the feasibility study required about 2-1/2 years to complete. While the percentage of the cost attributable to the feasibility study and its duration would undoubtedly be reduced in future applications of the Biocraft/GDS system at other sites, it illustrates the relative investment which may have to be put into the feasibility study (i.e., Steps II through VII of Figure 6-1) prior to startup of an in situ treatment application. Note that this figure ($446,280) does not include the RI portion ($73,948 or 8%) of the project nor does it include the engineering design portions ($119,891 or 13%) of the overall capital cost.

Independent of the particulars at the Biocraft Site, this discussion illustrates that application of an in situ treatment system is likely to involve a significant research and development component which will be site specific, possibly requiring a lengthy development period and possibly involving expenditures which will be a large fraction of the total capital cost.

TABLE 6-2

COSTS OF REMEDIAL ACTION AT THE BIOCRAFT SITE
(Cost Data From USEPA, 1984c)

Project Element	Expenditure
1. Activities Associated With Remedial Investigation (Step I, Figure 6-1)	
a. Monitoring Wells and Test Borings Installation	$ 6874
b. Laboratory Testing (Independent Laboratory plus 400 hrs Biocraft Time @ $50/hr)	$ 27704
c. Consultant Charges (including 200 hrs of Biocraft time, unit cost not specified)	$ 39370
Total RI Costs	$ 73948
2. Activities Associated With Feasibility Studies (Steps II - VII, Figure 6-1)	
a. Labor (including in-house labor)	$ 296280
b. Equipment	
i) Pilot Plant (building, piping, pumps)	$ 40000
ii) Other	$ 60000
Total Equipment	$ 100000
c. Quality Control Lab	$ 50000
Total Feasibility Study Costs	$ 446280
3. Implementation Costs	
a. Biostimulation Plant Design and Construction	
i) Engineering Design	
- Biocraft in-house (360 hrs @ $50/hr)	$ 18000
- Engineering, Drafting	$ 40400
Total Biostimulation Plant Design	$ 58400

ii) Masonry and Construction	$ 73975
iii) Equipment	$ 88832
Total Biostimulation Plant Costs	$ 221207
b. Delivery/Recovery System Design and Construction	
i) Design	
- Laboratory Testing	$ 10418
- Labor (consultants $24673; Biocraft in-house $26400)	$ 51073
Total Delivery/Recovery Design	$ 61491
ii) Installation (All Contractor Costs)	
- Air and monitoring well points	$ 12740
- Trenches, air well construction and site work	$ 80500
- Supervising Geohydrologist	$ 21513
- Engineering	$ 8000
Total Delivery/Recovery Installation	$ 122753
Total Delivery/Recovery Systems Costs	$ 184244
4. Operating Costs ($ per day)	
a) Utilities	
- Electricity (26.4 Kw, 24 hrs/day)	$ 46.82
- Steam (72 lbs/day @ 90 PSI)	$ .58
Total Utilities	$ 47.40

b) Maintenance Costs

- Quality Control Laboratory (technician)	$ 24.40
- Fermentation Laboratory (technician)	$ 97.10
- Maintenance	$ 20.26
- Supervision	$ 17.14
Total Maintenance	$ 158.90
c) Nutrient Salts	$ 19.20
Total Daily Operating Costs	$ 225.50

Cost per gallon: \$225.50/13680 gal/day = \$0.0165/gallon

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APPENDIX A

BIOLOGICAL DEGRADATION OF ORGANIC MATERIALS

APPENDIX A
EVALUATION OF SYSTEMS TO ACCELERATE STABILIZATION OF WASTE PILES OR DEPOSITS

BIOLOGICAL DEGRADATION OF ORGANIC MATERIALS

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES*
Acyclic hydrocarbons alkanes methane	Oxidation	CO_2, H_2O	Methylotropic bacteria in soils	aerobic, landfills, natural gas leaks	40-50% ± 10% V/V		68
N-alkanes (C_2 to C_{44})	Oxidation-oxidases and dehydrogenases	Monoterminal oxidations to primary alcohols; to aldehydes; and to monocarboxylic acids	Microorganisms				6, 59, 75, 100, 114
ethane	Cooxidations while grown on methane	Acetic acid, ethanol, acetaldehyde, CO_2, cell material and extracellular constituents	*Pseudomonas methanica*	aerobic, growth on methane	5% ethane, 45% methane, 50% air		79
propane	Cooxidations while grown on methane	Propionic acid, propanol, acetone, CO_2, cell material and extracellular constituents	*Pseudomonas methanica*	aerobic, growth on methane	30% propane, 40% methane, 30% air		79
	Oxidation of propane		*Mycobacterium vaccae*	aerobic			79
butane	Cooxidations while grown on methane	Butyric acid, 1-butanol 2-butanone	*Pseudomonas methanica*	aerobic, growth on methane			79
N-dodecane (C-12)	Cooxidations while grown on acetate	1,12 dodecanidoic acid	*Candida cloacae*	aerobic, growth on acetate	5% V/V		79
N-tridecane (C-13)		1,13 tridecanidoic acid			5% V/V		
N-hexadecane (C-16)		1,16 hexadecanidoic acid			5% V/V		
N-dodecane + N-hexadecane		1,12 dodecanidoic acid + 1,16 hexadecanidoic acid			5% V/V		
N-tridecane + N-hexadecane		1,13 tridecanidoic acid + 1,16 hexadecanidoic acid			5% V/V		
N-octadecane (C-18)	Esters produced via cooxidations of an n-Alkane substrate to a homologous oxygenated compound without degradation	$CH_3(CH_2)_{16}-COOCH_2-(CH_2)_{16}-CH + CH_3-COOCH_2-(CH_2)_{16}-CH_3$ (1:1 mixture)	*Micrococcus cerifecans*	aerobic, growth on alkane substrates			79
					Saturated soils		3, 6, 115

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* References listed following Section 2 of this report

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
N-hexadecane (C-16)		$(CH_2)_{14}$-$COOCH_2$-$(CH_2)_{16}$-CH_3 CH_3-$(CH_2)_{14}$-$COOCH_2$-$(CH_2)_{14}$-CH_3					
N-tetradecane (C-14)		CH_3-$(CH_2)_{14}$-$COOCH_2$-$(CH_2)_{12}$-CH_3					
N-dodecane (C-12)		CH_3-$(CH_2)_{14}$-COO-X (unknown)					
gasoline	Oxidation	CO_2, H_2O hydroxyperoxides, alcohols, aldehydes, ketones and esters	Soil bacteria	Surface and subsurface soil and groundwater contamination, H_2O_2 injection, aerobic and anaerobic respiration, fermentations			3, 66
petroleum	Oxidation, cooxidation beta, omega, alpha oxidation of mono and dicarboxylic acids, ring cleavage followed by oxidation, etc., of acyclic structure	CO_2, H_2O, alcohols, carbonyls, aldehydes, ketones and esters	Soil bacteria	aerobic and anaerobic respiration, fermentation			3, 6, 50, 66 77, 111, 113
			Salt water bacteria				
						16 days	73
			Mutant bacteria	Oil spill on beach sea temperature about 10°C air temperature 11°C sand sprayed with sea water twice daily. aerobic, nitrogen and phosphorous nutrients			114
lube oil							114
#2 fuel oil							114
#5 fuel oil							114
heavy main diesel							114
crude petroleum condensate							114
linear paraffins							
Branched Alkanes							
isopronoid alkanes	Omega oxidation	Dicarboxylic acids	Soil bacteria	aerobic			6
pristane methyl branching	Omega or alpha oxidation; or beta alkyl group removal	Mono and dicarboxylic acids	Soil bacteria	aerobic			6
isobutyl isobutyrate							
alkenes	Terminal oxidations subterminal dehydrogenation, splitting of carbon chain	Carboxylic acids, unsaturated acid, hydroxy acid and alcohol	Bacteria	aerobic			114 6
1 octene	Cooxidation to corresponding epoxide	1,2-epoxyoctene	Pseudomonas oleovorans Pseudomonas aeruginosa	aerobic	2 to 80 Percent (V/V)		26
1 hexadecene		1,2-epoxyhexadecane	Candida lipolytica, Corynebacterium equi	aerobic			26
Palmitoleic acid	Epoxidates internal double bond		Bacillus megaterium	aerobic, 30°C			26
1, 7-octadiene	Cooxidation	7,8-epoxy-1-octene and 1, 2-7, 8-diepoxyoctane	Pseudomonas oleovorans	aerobic two phase with fermentation cyclohexane		80% molar conversion	26
polyisobutylene			Mutant bacteria				114
diisobutylene			Mutant bacteria				114

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
Saturated alkyl halides							
bromochloromethane	anaerobic respiration, reductive dechlorination	CO_2 CH_4, H^+, Br^- and Cl^-	Soil bacterium, methanogenic mixed culture with acetate as substrate in sewage sludge	anaerobic, continuous flow fixed film reactor	37 ug/l	2 days	57
bromodichloromethane	Partial chem. transformation (Br) reductive dechlorination			anaerobic, continuous flow fixed film reactor	66 ug/l	2 days	13, 15
bromoform	anaerobic dechlorination partial chem. transformation (Br)						14, 57
chlorinated hydrocarbons	reductive dechlorination, anaerobic and aerobic respiration	CO_2, CH_4, H^+, Cl^-	Bacteria, BI-CHEM GEC-1, BI-CHEM POB-6 and BI-CHEM PEP-7	anaerobic, aerobic			2, 13, 14, 26, 45, 59, 71
carbon tetrachloride	reductive dechlorination, anaerobic respiration cooxidation	CO_2 CH_4, H^+ and Cl^-	Methanogenic mixed culture with acetate as substrate	anaerobic, continuous flow fixed film reactors, denitrification	54 ug/l	16 days	13, 14
chloroacetic acid	Dehalogenation, oxidation		Sewage bacteria			50% in 2 days	45
chloroacetate	Dehalogenation, oxidation Beta	CO_2, Cl^-	*Pseudomonas* sp.	aerobic, 29°C	47 ug/ml	10 days	12
chlorobutyric acid	Dehalogenation oxidation		Sewage bacteria				45
chloroethane	reductive dechlorination		Soil bacteria	anaerobic			57
chloroform	reductive dechlorination, anaerobic respiration cooxidation		Methanogenic mixed culture with acetate as substrate	anaerobic, continuous flow fixed film reactor	50 ug/ml-60 ug/l	30 days	13, 15, 71
2-chloropropionic acid	Dehalogenations, oxidation		Sewage bacteria			35%, 2 days	44
dibromochloromethane	reductive dechlorination anaerobic respiration, partial chem. transformation (Br) cooxidation		Methanogenic mixed culture with acetate as substrate, soil bacteria, sewage sludge	anaerobic, continuous flow fixed film reactor, denitrification	63 ug/l	2 days	13, 14, 15
dibromomethane	Dehalogenation		Soil bacteria	Anaerobic			57
dibromoethane	Partial chem. transformation (Br), anaerobic respiration cooxidation			Anaerobic, continuous flow fixed film reactor, denitrification	78 u g/l	2 days	13, 14
dichloroethane	Reductive dechlorination, anaerobic respiration cooxidation	CO_2, CH_4, H^+ and Cl^-	Soil bacteria, methanogenic mixed culture with acetate as substrate	Anaerobic, continuous flow fixed film reactor			57
1,2-dichloroethane							13
dichlofop-methyl	Reductive dechlorination decarboxylation		Bacteria				2
methyl chloride	Reductive dechlorination		Soil bacteria	Anaerobic			57 2
N-serve	Dehalogenation		Soil bacteria				2
propachlor	Dehalogenation		Soil bacteria, microbial culture				57
trichloroethane			Marine bacteria, sewage sludge	Aerobic, anaerobic		8 weeks	13, 15
1,1,1-trichloroethane	Reductive dechlorination, anaerobic respiration cooxidation		Methanogenic mixed culture with acetate as substrate	Anaerobic, continuous flow fixed film reactor, denitrification	53 u g/l	8 weeks	13, 15, 57

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
1,1,2,2-tetrachloroethane	Reductive dechlorination, anaerobic respiration cooxidation		Methanogenic mixed culture with acetate as substrate	Anaerobic, continuous flow fixed film reactor, denitrification			
trichloromethane	Reductive dechlorination, anaerobic respiration	CO_2, CH_4, H^+ and Cl^-	Methanogenic mixed culture with acetate as substrate	Aerobic, anaerobic continuous flow fixed film reactor, denitrification			13, 15, 57
tetrachloromethane	Reductive dechlorination, anaerobic respiration cooxidation		Methanogenic mixed culture with acetate as subtrate	Anaerobic, continuous flow fixed film reactor			13, 57
trichlorofluoromethane	Reductive dehalogenation		Sewage sludge	Anaerobic			57
methylene chloride	Dechlorination, oxidation		Soil bacteria	anoxic conditions			57
Unsaturated Alkyl Halides							
1,1-dichloroethylene	Dechlorination, oxidation		Sewage sludge BI-CHEM GEC-1	Aerobic (?)			57, 59
1,2-dichloroethylene	Dechlorination, oxidation		Sewage sludge BI-CHEM GEC-1	Aerobic (?)			57, 59
1,2-transdichloroethylene	Dechlorination, oxidation		Sewage sludge	Aerobic (?)			57
1,3-dichloropropylene	Dechlorination, oxidation		Sewage sludge	Aerobic (?)			57
Heptachlor	Epoxidation		Microbial culture, soil bacteria				2
perchloroethylene			PHENOBAC	aeration basin			114
trichloroethylene	Reductive dechlorination, anaerobic respiration, oxidation	CO_2, CH_4, H^+ and Cl^-	Methanogenic culture	Anaerobic		8 weeks	13, 15, 57
tetrachloroethylene	Reductive dechlorination, anaerobic respiration, oxidation	CO_2, CH_4, H^+ and Cl^-	Methanogenic culture	Anaerobic		8 weeks	13, 15, 57 57
vinylidiene chloride			Soil bacteria	anoxic conditions			114
Ethers, Glycols, Epoxides isopropyl ether							57
bis-(2-chloroisopropyl) ether			Sewage sludge	Aerobic			26
1, 2-epoxyoctane	Hydroxlation of free methyl group, beta oxidation		Pseudomonads sp.	Aerobic			
glycidol	Oxidation	CO_2, H_2O; CO_2, CH_4, and H^+	Activated sludge microorganisms, digester microorganisms	Aerobic, 30°C; Anaerobic, 37°C	100 ppm		50
ethylene glycol	Oxidation	CO_2, H_2O, glycolic acid, pyruvate to CO_2 and H_2O	Salt requiring bacterium T-52, Acetobacter sp., Gluconobacter sp., Acenitobacter sp.	Aerobic, 30°C	10.5 g/l	36 hours	20 20 20
glycidyl nitrate	Oxidation	Glycerol to CO_2, H_2O	Activated sludge microorganisms, digester microorganisms	Aerobic, 30°C; Anaerobic, 37°C	100 ppm		50
glycerol	Oxidation	Pyruvate to CO_2, H_2O, CH_4	Activated sludge microorganisms, digester microorganisms	Aerobic, 30°C; Anaerobic, 37°C	100 ppm		20, 50
polyethylene glycol	Polyethylene glycol dehydrogenase		Bacterial culture	Aerobic			95

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
Alcohols							
methanol	Oxidation	CO_2, H_2O	PHENOBAC, soil and methanol oxidation bacteria (*Methylococcus* and *Methylomonas*)	Aerobic			69, 75
arcenol	Oxidation		PHENOBAC				75
isobutyl alcohol	Oxidation		PHENOBAC				75
iso-nonyl alcohol	Oxidation		PHENOBAC				75
2-ethyl hexanol	Oxidation		PHENOBAC				75
decyl alcohol	Oxidation		PHENOBAC				75
N-propyl alcohol	Oxidation		PHENOBAC				73
tert butyl alcohol	Oxidation		PHENOBAC				75
octyl alcohol	Oxidation		PHENOBAC				75
isopropyl alcohol	Oxidation		PHENOBAC				75
polyvinyl alcohol	Oxidation	PVA oxidase degradation by successive reactors	*Pseudomonas putida* VM15A *Pseudomonas* sp. VM15C	Bacterial symbiotic relationship, aerobic, 30°C			93
Aldehydes and Ketones							
formaldehyde	Oxidation		PHENOBAC	Spray and leachate recirculation, aerobic, Bioreactor	1400 ppm	22 days	75, 114
acetone	Oxidation		PHENOBAC	Aerobic, digester, land farming		1 day	75
methyl ethyl ketone			PHENOBAC	Aerobic, digestion, land planning		1 day	75
acetaldehyde	Oxidation	Pyruvate to CO_2					98
acrolein							75
methyl-isobutyl-ketone							75
Carboxylic Acids							
orotic acid	Oxidation	CO_2 and H_2O	Bacteria	Aerobic, anaerobic			100

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCE
monocarboxylic acids to n-C44	Degradation of carboxylic acids proceeds by beta oxidation with the formation of acetyl-CoA, and a fatty acid shortened by a 2 carbon unit. Acetyl-Co A is metabolized to CO$_2$ and H$_2$O in the citric acid cycle	CO$_2$ and H$_2$O	Bacteria, Pseudomonads sp.	Aerobic, anaerobic			6, 99
Short & long chain acids		CO$_2$ and H$_2$O	Brevebacterium sp.	Aerobic			7
C$_{16}$-C$_{18}$ carboxylic acids		CO$_2$ and H$_2$O	Flavobacterium sp.	Aerobic, anaerobic			
dicarboxylic acids		CO$_2$ and H$_2$O	Mycobacterium vaccae				56
branched dicarboxylic acids			Pseudomonas sp.				77 77
pentanoic acid		CO$_2$ and H$_2$O	Soil bacteria as innoculum	Degradation of organic acids in shale oil retort water, aerobic, 24°C			77
hexanoic acid							86
heptanoic acid							86
octanoic acid							86
nonanoic acid							86
pr[illegible]anedioic acid							86
but[illegible]edioic acid							86
2-methylbutanedioic acid	Catabolism can require omega (diterminal) oxidation for dicarboxylic acids and alpha oxidation or beta alkyl group removal for branched chains			Degradation of organic acids in shale oil retort water, aerobic, 24°C			86
pentanedioic acid					30.9 ppm as C		86
hexanedioic acid					16.2 ppm as C	95% reduction in 21 days	86
heptanedioic acid					1.8 ppm as C		86
octanedioic acid					5.2 ppm as C		86
nonanedioic acid					7.4 ppm as C		86
decanedioic acid					9.9 ppm as C	80-90% reduction in 9 days	86
undecanedioic acid					9.9 ppm as C		86
tridecanedioic acid					9.5 ppm as C		86
tetradecanedioic acid					7.5 ppm as C		86
dodecanedioic acid					2.6 ppm as C		86
benzoic acid					8.8 ppm as C		86
Amides					20 ppm as C		86
acetamide	Hydrolase	Acetate to CO$_2$, ammonia to protein	Pseudomonas aeruginosa	Aerobic			77
Esters							
methyl acetate	Degradation						114
ethyl acetate							114
amyl acetate							114
diethyl adipate							114
dibasic esters							114
trimethylamine			BI-CHEM CEC-1				59
diethylamine	Biodegradation	CO$_2$	Pseudomonas sp.				11
diethanolamine	Biodegradation	CO$_2$	Pseudomonas sp.	Aseptic culture incubated aerobic, at 29°C, in the dark			11
dimethylamine	Biodegradation	CO$_2$	Pseudomonas sp.		210 mg/l	30% in 4 days	11
Phthalate Esters							
m-phthalic acid	Esterases		Mixed culture bacteria	Anaerobic, denitrifying conditions;			1
o-phthalic acid	Oxidation		Mixed culture bacteria	Aerobic, by Acenetobacter sp.			1
p-phthalic acid			Mixed culture bacteria				1
dibutyl phthalate							1
monobutyl phthalate			Nocardia sp.				1
terephthalic acid			Mixed culture	Anaerobic denitrifying conditions			1
di-n-butylphthalate	Esterases, oxidation		Pseudomonas sp. Pseudoalcaligenes sp.	Anaerobic denitrifying conditions			8, 86
di-(2-ethylhexyl) phthalate	Esterases, oxidation, capable of metabolizing other phthalate esters as well		Fresh water and marine phthalic acid ester degrading bacteria	Aerobic, 22°-25°C			107
n-dibutyl phthalate	Oxidation		Microorganisms				111
di-n-octyl phthalate							
dimethyl phthalate	Esterase, oxidation		Gram negative and gram positive bacteria	Aerobic, mesophylic temperature			107
diethyl phthalate							108
dibutyl phthalate							108

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
butylglycocyl butylphthalate							108 108
butylbenyl phthalate							108
diisobutyl phthalate							114
di-isononylphthlate							111
phthalate esters	Second order microbial degradation rate constants						
Nitrosamines							57, 58
dimethylnitrosamine		Nontumorigenic product	*Rhodopseudomonas capsulata*, rumen organisms	Anaerobic, acetate pH 27°C illumenated	1.1 ug/ml	20 days	113
n-nitrosodiethanolamine (NDEIA)	Mineralized	Not identified but suggested to be non-carcenogenic dimers of NDEIA	Lake water and sewage bacteria	Lake water pH 4.8 and 7.8 sewage pH 7.8 seasonal effect in lake water			15
Thiols ethanethiol benzenethiol	Biodegradation		Bacteria				
Cyclic Alkanes							79
cycloalkanes	Mineralization	CO_2	Mixed microbial population				26
cyclohexane	Oxidation	CO_2, H_2O	*Pseudomonas oleovorans*	Aerobic, fermentation			79
cyclohexane	Cooxidations, commensalism	Cyclohexanone, metabolized to $CO_2 + H_2O$	*Mycobacterium vaccae*,	Growth on propane substrate			79
n-hexane	Cooxidations, commensalism	Cyclohexanol used by second organism as a source of carbon and energy	Two *Pseudomonas* sp.				
cycloparaffins cyclopropane cyclopentane methyl cyclopentane 2-cyclopentene cyclohexane cycloeptane cyclooctane	Cooxidations, commensalism with other soil microorganisms utilize products as sources of carbon and energy	 Propaldehyde Cyclopentone Methyl cyclopentone Cyclopentanone Cyclohexanone Cyclosiptanone Cyclooctanone	*Mycobacterium vaccae* and other soilm icroorganisms				79 79 79 79 79 79 79 79
n-butyl cyclohexanol	Cooxidation	Cyclohexaneacetic acid	*Nocardia* sp.	Growth on n-alkanes			43
Nitriles, cyanides							
acrylonitrile			Mixed culture of yeast mold, protozoa bacteria; activated sludge	Aerobic			57
acetonitrile	Degradation		Mutant microorganism	20°C	500 mg/l	100% in 3 hrs	61, 75, 114
acrylonitrile	Degradation		Mutant microorganism Mutant microorganism	20°C biotreator	500 mg/l 100 ppm-1000 ppm	100% in 3 hrs 1 ppm, 3 months	61, 75, 114 61, 75, 114
adiponitrile							
phenylnitrile	Degradation		Mutant microorganism	20°C	500 mg/l	100% in 10 hrs	61, 75, 114
phthalonitrile	Degradation		Mutant microorganism	20°C	500 mg/l	100% in 16 hrs	61, 75, 114
hydrocyanic acid	Degradation		Mutant microorganism	20°C	250 mg/l	100% in 1 hrs	61, 75, 114
sodium cyanide	Degradation		Mutant microorganism	20°C	250 mg/l	100% in 3 hrs	61, 75, 114
dichlorophenyl isocyanate	Degradation		Mutant microorganism	20°C	500 mg/l	100% in 8 hrs	61, 75, 114
cyanides, cyanates			BI-CHEM CS-1-9				59

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
Amines							
analine	Degradation		Mutant *Aerobacter* sp.		500 mg/l	100% in 10 hrs	61, 75, 114
diethylaneline							
o-chloroaneline	Degradation						114
p-chloroaneline	Degradation		Mutant *Aerobacter* sp.		500 mg/l	100% in 20 hrs	61, 75, 114
4-chloroaneline	Dechlorination		Mutant *Aerobacter* sp.		500 mg/l	100% in 18 hrs	61, 75, 114
trichloroaneline	Degradation		Sewage microflora				44
Aromatic hydrocarbons			Mutant *Aerobacter* sp.		500 mg/l	100% in 30 hrs	61, 75, 114
aromatics							
alkyl benzene sulfonate	Cooxidation in the presence of glucose followed by complete metabolism of end products	Isopropanol & catechol both used as growth substrates	*Pseudomonas* sp.	Aerobic, pure culture		100% in 20 days	6 43
benzene	Ortho (intradiol) pathway mono & dioxygenase	CO_2	Bacteria	Aerobic, molecular O_2 is essential			31
	Meta (extradiol) pathway - hydration or hydrogenation followed by nonoxidative ring fission	CO_2	Bacteria	Anaerobic			31
			Pseudomonas putida,	Aerobic			57
			Sewage sludge	Aerobic			57
			Stabilization pond microbes	Aerobic (?)			57

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
benzoate	Photometabolism - reduction by a novel pathway leading to ring fission	Pimelate	*Rhodopseudomonas palustris*	Anaerobic, photosynthetic conditions	20 u moles	90 minutes	29
	Mandelate pathway	Succinate and acetyl-CoA by citric acid cycle to CO_2 & water	*Pseudomonas putida*	Aerobic			77
	Mineralization		Fresh water bacteria, sewage	Aerobic	59,000 pg/ml	99% in 9 days	89
	3-oxoadipate benzoate pathway		*Pseudomonas* sp. B13 Transconjugant *Alcaligenes* sp. strain A 7-2 transfer of halocatechol-degrading capacity from *Pseudomonas* sp. B13	Aerobic			90
	Oxidation			Aerobic, low sensitivity to phenols, 28°C on shaker culture			91
benzoic acid	Microbial degradation of oil shale retort water	CO_2	Mixed population of soil bacteria	Aerobic, phosphate supplement	21 ppm as carbon	90% in 9 days	86
divinyl benzene			BI-CHEM GEC-1				59
hydroxy benzoate p-hydroxy benzoate	Aerobic metabolism 4,5-oxygenase pathway	Gamma carboxyl-alpha-hydroxy muconic semialdehyde and subsequent break down involving pyruvate	*Rhodopseudomonas* sp.	Aerobic			29
p-hydroxy benzoate	Beta-ketoadipate pathway	Succinate and acetyl-Co A metabolize to CO_2 and H_2O in citric acid cycle	*Pseudomonas putida*	Aerobic			77
2,4 dihydroxy benzoate	Photoassimilation		*Rhodopseudomonas palustris*	Anaerobic, growth on benzoate in light	20 u moles	240 minutes	29
dihydroxy benzoate	3-oxoadipate pathway dehydroxybenzoate dehydrogenase		*Pseudomonas* sp. B13	Aerobic			90
3 methyl benzoate			*Pseudomonas* sp., sewage	Aerobic, plasmid transfer led to the ability to use this compound as a sole energy and carbon source			57
benzyl formate	Mandelate pathway	Benzoate which is degraded by the beta-ketoadipate pathway to acetyl-CoA and succinate (metabolites) of the citric acid cycle	*Pseudomonas putida*	Aerobic			77
cis-cis-muconate	Oxidation		*Rhodopseudomonas palustris*	Aerobic, growth on p-hydroxy benzoate			29
	muconate-cycloisomerase		*Pseudomonas* sp.	Aerobic			90
n-butylbenzene	Cooxidation	Phenylacetic acid	*Nocardia* sp.	Growth on N-alkanes			43
ethylbenzene	Cooxidation	Phenylacetic acid	*Nocardia* sp.	Growth on N-alkanes			43
n-propylbenzene	Cooxidation	Cinnamic acid	*Nocardia* sp.	Growth on N-alkanes			43
3-methylmuconic acid	Muconate-cycloisomerase		*Pseudomonas* sp. B13	Aerobic			90
p-isopropyltoluene	Cooxidation	p-isopropylbenzoate	*Nocardia* sp.	Growth on N-alkanes			43
pyrolidone		Glutamic acid	*Bacillus* sp.				43
toluene			*Bacillus* sp. *Pseudomonas putida*	Anaerobic Aerobic			57
o-xylene	Cooxidation	o-toluic acid	*Nocardia* sp.				43
p-xylene	Cooxidation	p-toluic acid,2,3-dehydroxy-p-toluic acid	*Nocardia* sp.				43
tri-p-cresyl phosphate	Oxidation	CO_2	Activated return sludge	Aerobic, 21°C	1 u g/ml	70-80%, 24 hrs	62

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
Halogenated Aromatics							
alpha chlorotoluene	Dechlorination		Sewage microflora			$17\ ng/l^{-1}/hr^{-1}$, (upstream)	45
chlorobenzene	Respiration	CO_2	Heterotrophic bacteria	Aerobic, 27°C to 6°C		$14\ ng/l^{-1}/hr^{-1}$, (estuarine) $0.03\ ng/l^{-1}/hr^{-1}$ (marine)	44
3-chlorobenzoate	Dechlorination		Sewage microflora				45
	Dechlorination, growth		Pseudomonas sp. B13				
	Dechlorination, growth		Alcaligenes sp. A7-2				
p-; m-; o-chlorobenzoate 1,2-;2,3-;1,4-dichlorobenzene 3,4-;3,5-dichlorobenzoate	Use as sole carbon sources		Pseudomonas sp.	Plasmid transfer led to ability to metabolize these compounds simultaneously; sole energy and carbon source			27, 57
m-dichlorobenzene	Degradation, ring disruption		Mutant Pseudomonas sp.	Aerobic, 30°C	200 mg/l	100% 29 hrs	61, 75, 108 114
o-dichlorobenzene	Degradation, ring disruption		Mutant Pseudomonas sp.	Aerobic, 30°C	200 mg/l	100% 26 hrs	61, 75, 108 114
p-dichlorobenzene	Degradation, ring disruption		Mutant Pseudomonas sp.	Aerobic, 30°C	200 mg/l	100% 25 hrs	61, 75, 108 114
3,4-dichlorobenzoate	Use as sole carbon source		Microbial population in sewage	25°C, dissolved O_2 at 6-8 ug/ml	100 ug/ml	9 days	27
2-;3-;4-fluorobenzoic acid	3 chlorobenzoate grown cells readily cometabolized	Benzoate pathways used 2 fluoro-cis-cis-muconic acid dead end metabolic product of 2- and 3-fluorobenzoate	Pseudomonas sp. B13				90
	Monofluorobenzoates	Complete metabolism of 4-fluorobenzoate occurs					
hexachlorobenzene			Sewage sludge mutant	Aerobic			57
monochlorobenzene	Degradation, ring disruption		Pseudomonad sp.	Aerobic, 30°C	200 mg/l	100%, 15 hrs	61, 75, 108, 114
monochlorobenzoate	Cometabolism		Nocardia sp., mycobacterium	Aerobic			57
trichlorobenzene			Sewage sludge	Aerobic			57
1,2,3- and 1,2,4-trichlorobenzene		2,6-; 2,3-dechlorobenzene, 2,4- & 2,5 dichlorobenzene; CO_2; slow	Soil microbes	Aerobic			57
1,3,5-trichlorobenzene	Degradation, ring disruption		Mutant Pseudomonas sp.	Aerobic, 30°C	200 mg/l	100%, 52 hrs	61, 75, 108, 114
1,2,4-trichlorobenzene	Degradation, ring disruption		Mutant Pseudomonas sp.	Aerobic, 30°C	200 mg/l	100%, 48 hrs	61, 75, 108, 114
	Biodegradation	CO_2	Soil bacteria	Aerobic, 20°C, 66% moisture, fertilizer	500 ppm/g		69
	Biodegradation		Newport River, N. Carolina microbial community	Fresh, brackish and marine water; 30°C	Dry weight soil	$9.1\ ng/l^{-1}/hr^{-1}$	80
1,2,3-trichlorobenzene	Degradation, ring disruption		Mutant Pseudomonas sp.	Aerobic, 30°C	200 mg/l	100%, 40 hrs	61, 75, 97, 114
	Biodegradation	CO_2	Soil bacteria	A, 20°C, 66% moisture fertilizers			69
2,3,6-trichlorobenzoate	Dechlorination, cometabolism, inducable enzyme induction	3,5-dichlorocatechol	Brevibacterium sp.				43

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
Simple Aromatic Nitrogen compounds							
4-aminobenzene	Ring clevage, possible mineralization		Sewage	Aerobic			40
hexahydro-1,3,5-trinitro-1,3,5-triazine	Biodegradation, successive reduction of nitro groups to a point where destabilization and fragmentation of the ring occurs. Non cyclic degradation products arise via subsequent reduction and rearrangement of reaction products.	Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine, hexahydro-1,3-dinitroso-5-nitro-1,3,5-trinitroso-1,3,5-triazine,hydrazine,1,1-dimethyl-hydrazine,1,2,-dimethylhydrazine, formaldehyde, and methanol	Activated sludge	Anaerobic, denitrification	500-100 ug/ml	4 days	72
nitrobenzene			Stabilization pond microbes	Aerobic (?)			57
	Ring clevage, possible mineralization	Analine	Sewage	Aerobic			40
3- and 4-nitrobenzoic acid		Aminobenzoic acid	Sewage	Anaerobic or aerobic			40
1, 2- and 1,3-dinitrobenzenes		Nitroanaline	Sewage	Anaerobic or aerobic			40
3,5-dinitrobenzoic acid		Aminonitrobenzoic acid	Sewage	Anaerobic or aerobic			40
2,4-dinitrotoluene			Stabilization pond microbes	Aerobic (?)			57
2,4,6-trinitrotoluene		2-amino-4,6-dinitrotoluene; 4 amino-2,6-dinitrotoluene; 2,4-diamino-6-nitrotoluene; 2,6-diamino-4-nitrotoluene; 2,2,6,6-tetranitro -4,4 azoxytoluene; 2,4,6,6-tetranitro-2,4-azoxytoluene	Thermophilic microorganisms	Aerobic, composting systems, 55°C, 60% moisture		91 day composting	51
Aromatic Nitro compounds with Other Functional Groups							
benzylamine	Mineralization		Lake water bacteria		1 u g/ml	500 ng/ml^{-1}/hr^{-1}	89
	Mineralization		Lake water, sewage		250 ng/ml or less	590 pg/ml^{-1}/hr^{-1}	104
	Mineralization		Lake water or sewage		284 pg/ml	60 hours	105
4-chlorobenzonitrite	Dechlorination		Sewage microflora				45
4-chloro-3,5-dinitrobenzoic acid	Dehalogenation, cometabolism	Alpha-hydroxymuconic semialdehyde mineralized by *Streptomyces* sp.	*Chlamydomonas* sp. A1 and A2, sewage microflora	In the light in the absence of nutrients and in the dark with acetate			45
4-chloro- 2,5-dinitrobenzoic acid	Dehalogenation		Sewage microflora				45
3-and 4-nitrotoluenes		Toluidine	Sewage	Anaerobic			40
2,6-dinitrotoluene		Aminonitrotoluene	Sewage	Aerobic, anaerobic			40
4-toluidine	Degradation		Sewagr	Aerobic			40
Phenols							
camphor	Monooxygenases oxidation	3,4,4; trimethyl-5-carboxymethyl delta 2-cyclopentone metabolized to isobutyrate, converted to isobutyl-CoA which is metabolized via valine catabolism	*Pseudomonas putida*	Aerobic, inducible enzyme systems			77
cinerone	Cooxidation hydroxylation	Cinerolone	*Aspergillus niger*				43

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
cinnamate	Mineralized	CO_2 and CH_4	Sewage sludge	Anaerobic			31
	Mineralized	CO_2	Ground water bacteria, stream bacteria			20% in 500 hrs	63
diphenyl hydrazine			Sewage sludge	Aerobic			57 57
p,p-dichlorodiphenyl-methane	Cooxidation	p-chlorophenylacetate	Hydrogenomonas sp.	Aerobic			43
cresol		Used as carbon and energy source	Pseudomonas sp. Aureobasidium pullulans	Aerobic			
p-cresol	Mineralization	CO_2	Adapted site bacteria	Anaerobic, sediment and water of estuarine and marine sites 20°C	50 mg/l	70 hrs	99
creosotes			Microorganisms				28
methyl creosotenate	Mineralization		BI-CHEM GEC-1				59
ethoxylated phenols	Mineralization		BI-CHEM TEX-6				59
phenolics	Biodegradation		Microorganisms	Pits, ponds, lagoons soils and waste water			28
			BI-CHEM COL-1				59
	Degradation ring disruption		Mutant Pseudomonas sp.	30°C			61, 75, 108, 110, 114
phenol	Fermentation	To valerate, butyrate, propionate, acetate, formate and hydrogen. Organic acids fermented to CO_2 & CH_4	Bacterial consortia from a variety of methanogenic ecosystems.	Anaerobic			31
	Phenol degradation affected by iron concentration, bacterial innoculum size and pH		Oil refinery settling pond bacteria	Aerobic, shaker culture 28°C. Maximum degradation rate is 100 mg/liter with a pH optimum between 7 and 8. Continuous light.	100-400 mg/liter	34 to 100 hours	45
	Mineralization		Pseudomonas sp., Vibrio sp., Spirillum sp.	Aerobic			57
	Mineralization		Bacillus sp., Nocardia sp.	Aerobic			57
	Mineralization		Chlamydomonas ulvarensis	Aerobic, light required			57

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
	Mineralization		Phoridium fuvoolarum, Scenediamus beacilienses	Aerobic			57
	Mineralization		Euglene gracilus	Aerobic, light required			57
	Mineralization		Corynebacterium sp.	Aerobic			57
	Degradation, ring disruption	CO_2, water, cell protoplasm	Mutant Pseudomonas sp.	Aerobic, 30°C inorganic fertilizers (N and P)	500 mg/l	24 hrs	61, 75, 108, 11, 114
	Oxidation		Constructed strains of Pseudomonas sp. strain B13, Alcaligenes sp. strain A 7-2	Aerobic, 30°C, continuous culture			91
	Mineralization		Lake water bacteria sewage bacteria	Aerobic, 29°C, no illumination	Trace 1-100 ug/ml		89
	Oxidation, ortho pathway, phenol hydroxylase, catechol 1,2-oxygenase	Beta ketoadipate	Trichosporon cutanium PCB14	Aerobic, 30°C growth in a Marubishi jar fermentation	250 mg/l	100% 14 hrs	96
	Mineralization	CO_2	Freshwater and sewage bacteria	Aerobic, pH 7.0 ,29°C	trace		105
phenylphenol			BI-CHEM GEC-1				59
resorcinol			BI-CHEM GEC-1				59
Aromatics with Halogenated Side Chains							
1,1-diphenyl-2,2,2-trichlorothane	Cometabolism	3-phenyl-3,3,3, trichloropropionic acid	Brevibacterium sp.				43
p,p-dichlorodiphenyl-methane	Cometabolism	p-chlorophenylacetate	Hydrogenomonas sp.	Aerobic			43
2,4,5-trichlorophenoxy acetic acid	Cometabolism	3,5-dichlorocatechol	Hydrogenomonas sp.	Aerobic			43
styrene			BI-CHEM GEC-1				59
			BI-CHEM SUS-8, Detoxsol	Aerobic, Contaminated soil depth to 8 inches	25 ppm	1 ppm, 21 days	59
Halophenols							
pentachlorophenol	Oxidation use as sole source of organic carbon and energy	CO_2	Bacterium EC-3	Aerobic, continuous flow enrichment culture pH 7.5, 25°C	200 gm/l	73% in 24 hrs	24
			Soil microbes	Anaerobic			57
			BI-CHEM PEP-7				59
	Metabolized as sole carbon source	CO_2, cell mass	Arthrobacter sp. strain NC	Aerobic, chemostat	500 u g/ml	97% reduction	101
monochlorophenol	Cometabolism		Nocardia sp., Mycobacterium sp.	Aerobic			57
4-chlorophenol	Cometabolism		Pseudomonas sp. B13	Aerobic			90
4-chlorophenol	Sole energy and carbon source		Pseudomonas sp., sewage	Aerobic, use of plasmid transfer to enhance metabolism			57
	Oxidation, sole carbon and energy source		Pseudomonas, sp. strain B13,	Aerobic			91
	1,2-dioxygenation of chlorocatechols		Alcaligenes sp. strain				91
	Biodegradation		A7-2 mutant bacteria	Aerobic, pond leachates of phenols and o-chlorophenols	250 ppm	75% in 36 days	110
ortho chlorophenol			Mutant bacteria	Aerobic, contaminated soil and pond spray injection leachate system, biotreator pond	15,000 ppm	1 ppm, 9 months	114

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
dichlorophenylisocyanate	Degradation and disruption		Mutant *Pseudomonas* sp.	Aerobic, 20°C	500 mg/l	100%, 6 hours	61, 75, 108,
2,5-dibromophenol	Degradation and ring disruption		Mutant *Pseudomonas* sp.	Aerobic, 30°C	200 mg/l	100%, 37 hours	61, 75, 108,
m-bromophenol					200 mg/l	100%, 29 hours	
pentachlorophenol					200 mg/l	26%, 120 hours	
2,3,5-trichlorophenol					200 mg/l	100%, 58 hours	
2,5-dichlorophenol					200 mg/l	100%, 40 hours	
p-chlorophenol					200 mg/l	100%, 32 hours	
Nitrophenols							
nitrophenol	Nitroreduction	p-aminophenol	Rumen microorganisms	Anaerobic			57
p-nitrophenol	Mineralization	CO_2	Acclimated estuarine or marine bacterial communities (2-weeks adaption)		20-100 ppb		99
fenitrothion (O,O-dimethyl-O[3-methyl-4-nitrophenyl] phosphorothionate)	Cometabolism, can be used as sole carbon source		Lake Ontario sediments, soil & activated sludge	Anaerobic, cyclone fermentor		0.5-1 day	67
			Acinetobacter sp., *Aromonas* sp., *Bacillus* sp., *Pseudomonas* sp., *Flavobacterium* sp., etc.	Aerobic		0.5-1 day	67
Phenols-Dihydrides, Polyhydrides							
t-butyl catechol			BI-CHEM CEC-1				59
catechol	Oxidation	Beta ketoadipate, metabolized further to succinate and acetyl-Co A, then to CO_2 and H_2O	*Pseudomonas putida*	Aerobic			77
	Metabolism		*Pseudomonas* sp. B13	Aerobic			90
	Metabolism		*Alcalignes* sp. A7-2	Aerobic			91
chlorocatechol	Degradation		*Pseudomonas* sp. B13	Aerobic			90
4-chlorocatechol	Cometabolism, meta cleavage oxygenase	2-hydroxy-4-chloro-muconic-semialdehyde	*Achromobacter* sp.				43
3,5-dichlorocatechol	Cometabolism, meta cleavage oxygenase	2 hydroxy-3,5-dechloro-muconic-semialdehyde	*Achromobacter* sp.				43
	1,2 deoxygenase		*Alcaligenes* sp. A7-2				91
3,4-chlorocatechol	1,2 deoxygenase		*Alcaligenes* sp. A7-2				91
3-methylcatechol	Cometabolism	2-hydroxy-3 methyl-muconic semialdehyde	*Achromobacter* sp.				43
4-chlororesorcinol	Cometabolism		Sewage				44
protocatechuate	Oxidized protocatechuate; 4,5-oxygenase pathway	Supports growth	*Rhodopseudomonas palustres*	Aerobic			29
Polycyclic Hydrocarbons							
Two and Three Ring Fused Polycyclic Hydrocarbons							
anthracene	Microbial transformation	CO_2, nonextractable bound C (90%)	Stream sediments downstream of a coal coking wastewater discharge site	Aerobic, 20°C		64 days	38, 57
Aroclor 1221	Degradation		*Alcaligenes facalis*	Aerobic, 30°C		1-3 days	55
	Sole carbon source, degradation, commensurate growth		Plasmid harboring mixed cultures	Chemostat			38

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
biphenyl	Degradation, meta pathway degradation	Chlorobenzoic acid	*Acinetobacter* sp. P6 *Arthrobacter* sp. M5	Aerobic, plasmid involvement, 25°-30°C			38
			Alcaligines faccalis	Aerobic, 30°C		1-3 days	55
		Cis-2,3-dihydroxybiphenyl	*Beijerinckia* B8/36	Aerobic			57
		4-hydroxybiphenyl benzoic acid	*Oscillatoria* sp., *P. putida*	Aerobic			57
	Biodegradation	CO_2	Port Valdez, AK seawater-5 m depth	10°C, no aeration	4.7-4.4 u mole/liter	9.3-9.8 n mole/liter/day	85
chlorobiphenyl 4-chlorobiphenyl	Degradation	Chlorobenzoic acid	*Acinetobacter* sp. P6	Aerobic, plasmid involvement 25°-30°C		98% usage	38
mono and dichlorobiphenyls	Total degradation	CO_2, H_2O, Cl^-	*Arthrobacter* sp. with plasmid p AC27-or PAC31-harboring *Pseudomonas putida*			98% in 1 week	38
monochlorobiphenyls	Degradation		Port Valdez, AK, seawater 5 m depth	10°C, no aeration	1.5-4.5 u mole/liter	1.2-4.1 n mole/liter/day	85
mono and dichlorobiphenyls	Biodegradation		*Pseudomonas* sp., *Vibrio* sp., *Spirellum* sp., *Flavobacter* sp.	Aerobic			57
	High level dehalogenase	Major end product CO_2	*Achromobacter* sp., *Chromobacter*, sp., *Bacillis* sp., *Nocardia* sp.				57
4-chlorobiphenyl 4,4-dichlorobiphenyl dichlorobiphenyl		4-chloro-4 hydroxy biphenyl 4,4-dichloro-3-hydroxybiphenyl Chlorinated benzoic acid	Fungi				57
fluoranthene			Sewage sludge	Aerobic			57
naphthalene	Degradation	CO_2, unidentified yellow compound	Naphthalene utilizing microorganisms from soil	Aerobic, pH 7.0, shaker culture	100 mg/l	94%, 48 hrs	5
		Gentisate	*Pseudomonas* sp. A3 and *Pseudomonas* sp. C22	A, 30°C, biostat fermentors			17
	Oxidation	1-naphthol, 4-hydroxy-1-tetralone, cis-naphthalene dihydrodiol.	Cyanobacteria and microalgae	Photoautotrophic conditions			21
	Isomerization oxidation	cis-1,2-dihydroxy-1,2-dihydro naphthalene; 4-hydroxy-1-tetralone; and 1-naphthol	*Oscillatoria* sp. *strain JCM*	Photoautotrophic conditions			22
	Microbial transformation	CO_2, cell bound C	Stream sediments downstream from a coal coking wastewater discharge site sediment	Aerobic, 20°C		310 days	41
	Sediment absorbed biodegradation		Bacteria				56
			BI-CHEM FOG-3				59
		1-naphthol; cis-1, 2-dihydroxyl-1,2-dihydronaphthalene; 4-hydroxy-1-tetralene alpha-naphthol; beta-naphthol; trans-1,2-dehydroxy-1,2-dehydronapthalene; 4-hydroxyl-1-tetralene;1,4-naphtho quinone	*Agnenellum* sp., *Oscillatoria* sp., *Anabaena* sp., *Cunninghamella elegans*	Aerobic			57

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
	Ability to breakdown this compound common among algae		Microcoleus sp., Nostoc sp., Coccochloris sp., Aphanocapsa sp., Chlorella sp., Dunalilla sp., Chlamydomonas sp. Amphora sp.	Aerobic, light required			57
			Pseudomonas sp., Flavobacterium sp.,. Alcaligenes sp., Corgaibacterium sp. Aeromonas sp., Norcardia sp.	Aerobic			57
CH_3, OCH_3, Cl or NO_2 substituted naphthalenes	Degradation	Hydroxylated in 7,8 positions and 4-substituted salicylates are accumulated	Pseudomonas sp. A3 Pseudomonas sp. C22	Aerobic, 30°C, biostat fermentors			17
CO_2H, CH_2CO_2H or SO_3H substituted naphthalenes	Degradation	Hydroxylation in 1,2 position, 1,2-dehydroxy-1,2-dehydro naphthalene-2-carboxylic acids are formed	Pseudomonas sp. A3 Pseudomonas sp. C22	Aerobic, 30°C, biostat fermentors			17
napththalenesulfonate 1-naphthalenesulfonate 2-naphthalenesulfonate	Degradation	Unidentified end products which are metabolized by other bacteria	Pseudomonas sp. A3, Pseudomonas sp. C22. naphthalene degrading sewage bacteria	Aerobic, 28°C			16, 17
phenanthrene	Degradation		Alcaligenes faecalis, Beijerinckia Bwt, Pseudomonas SPM64	Aerobic, 30°C		2-3 days	55
	Degradation		Marine sediments				
		Cis-3,4-dehydroxy-3,4-dehydro phenanthracene	Beijerinckia sp.	Aerobic			56
	Biodegradation						57
polycyclic aromatic hydrocarbons	Biodegradation		Indigenous reservoir microbial population	25°C in dark	100 u g/100 mole	80%, 4 weeks	93, 94
	Degradation		Microorganisms	Pits, ponds, lagoons, soils and wastewater streams			28
	Biodegradation		Marine sediment bacteria	15°C, dark			56
polychlorinated biphenyls	Biodegradation		Indigenious reservoir microbial population	25°C, dark			94
	Biodegradation appears to be inversly related to extent of chlorination		Microorganisms	Pits, ponds, lagoons, soils and wastewater streams			28
			Pseudomonas sp. Vibrio sp., Spirillum sp., Flavobacterium sp.	Aerobic			57
Four Ring Fused Polycyclic Hydrocarbons							
Benz(a)Anthracene	Microbial transformation		Stream sediments in vicinity of coal coking wastewater discharge site	Aerobic, 25°C		34 days	41
dibenzanthracene		3,4-;8,9-;10,11-Dihydrols	Cunninghamella elegans	Aerobic			
chrysene	Degradation	Very slow insignificant breakdown	Activated sludge	Aerobic			57
polynuclear aromatics			Marine sediments	15°C, dark			57
	Biodegradation		BI-CHEM FOC-3				56
			Indigenous reservoir bacteria	25°C, dark		4 to 8 weeks	59 94

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
Five Ring Fused Polycyclic Hydrocarbons							
benzo(a)pyrene		Trans-7,8-dihydroxy-7,8-dihydrobenzo(a)pyrene	Cunninghamella elegans	Aerobic			57
			Pseudomonas sp. Beijerinckia sp.	Aerobic Aerobic			
Fused Polycyclic Hydrocarbons							
coal	Degradation, lignin digestion	Black liquid product	Polyporous versicola, Poria, monticola	Lignite coal, 28°C, 80% relative humidity			25
Organophosphates							
aapon	Used as sole phosphorous sources-none of the organo-phosphates served as a carbon source		Bacteria isolated from soil and sewage Pseudomonas pertida, Pseudomonas 28 Pseudomonas 7	Aerobic, 29°C shaker cultures			87
azodrin		Dimethyl phosphate					87
dasanit		diethyl phosphorothionate					87
desinon		diethyl phosphorothionate					87
malathin		dimethylphosphorodithioate					87
orthene							87
parathion		diethylphosphorothioate					87
trithion		diethylphosphorothioate					87
dimethoate							87
dylox							87
methyl parathion							87
vapona							87
parathion	Nitroreduction	Amino-parathion	Bacillus subtilus, Rhyzobrum sp., Chlorella pyrenordsa, soil bacteria	Anaerobic			57
	Ring cleavage mineralization	CO_2	Rice rhizosphere	Flooded and non flooded conditions		15 days	84
	Hydrolyses	Diethylthiophosphoric acid and p-nitrophenol	Pseudomonas diminuta				92
methyl parathion	Transformations		Aufwuchs microorganisms	Aquatic microbial growth attached to submerged surfaces or suspended in streamers or mats.			64
Pesticides and Herbicides							
trichlorophenoxyacetic acid (agent orange)	Degradation		Pseudomonas capecio AC 1100	Growth in soil, 30°C, 15-50% moisture	1 mg/gm soil	95%, 1 week	23, 52, 53
	Total degradation, sole source of carbon, 2,4,5-T degradation pathway		Microorganism from waste dump sites	Plasmids pAC 25, TOL, CAM, SAL pAC21; chemostat environment	800 u g/ml	70%, 7 days	51
	Dechlorination, oxidation	Cl^-, chlorophenols and related compounds	Pseudomonas capecia ACl 100	Aerobic, 30°C shaker culture	1 mg/ml	97%, 6 days	52
methoxychlor	Dechlorination	Cl^-, CO_2	Soil bacteria	Anaerobic, denitrifying conditions	1,000 ppm	90%, 3 months	37
	Bioaccumulation		Aerobacter aerogenes, Bacillus subtilis	Aerobic, shaker culture 25°C	0.5-5.0 u g/liter	30 minutes	46
			Nocardia sp., Streptomyces sp.	Aerobic			57
		1,1-dichloro-2,2-bis (p-methoxyphenyl) ethylene; 1,1-dichloro-2,2-bis (p-methoxyphenyl)-ethene	Aerobacter aerogenes	Aerobic, anaerobic			21
acrolein		Beta-hydroxypropionaldehyde	Site water microbes	Aerobic			57

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
chlorodimeform	Biodegradation, non enzymatic degradation	4-chloro-o-formotoluidilene, 4-chloro-o-toluidene, 5-chloro anthranilic acid, n-formyl-5-chloroanthranilic acid	Chlorella, Oscillatoria	Aerobic, 25°C, presence of light	960 u g/ml	14 days	9, 57
DDT	DDD		Anaerobic digestion, sludge	Anaerobic, 35°C			42
	Degradation	DDD, DDE, kelthane, DBP and DBM	Soil microorganisms	Anaerobic			39
	Reductive dechlorination	DDD	Commercial yeast	Anaerobic			49
	Reductive dechlorination	DDD	*Klebsiella pneumonia*, *Escherichia Coli* *Aerobacter aerogenes*, *Pseudomonas clostridum*, *Pseudomonas vulgaris*	Anaerobic, more than 20 bacteria species are reported to be able to R $DeCl_2$ DDT			57
		DDE		Aerobic			57
		DDM, DDMS, TDE, DDE	Oceanic conditions				78
diuron	Mineralization		Mixed culture of fungi and bacteria	Aerobic, anaerobic symbiotic relationship			57
dieldrin	Anaerobic degradation		Anaerobic digester sludge	Anaerobic, 35°C	150 u g/ml	Slow	42
		Photodieldrin, toxic epoxide moiety reduced to deflen	*Anacystis nidulans*, *Agmenelloum quardiplicatuns*, *Pseudomonas* sp.	Anaerobic			57
			Rumen fluid	Anaerobic			57
		Chlordine, chlordene epoxide	Actinomycetes	Anaerobic, aerobic			57
		Photodieldrin, aldren diol	Ocean sediments				78
aldrin	Degradation		Anaerobic digester sludge	Anaerobic, 35°C	1 ppm	10%, 40 days	42
	Epoxidation	Dieldrin	Site water microbes, sewage sludge				57
	Degradation	Aldrin diol, photodieldrin	Sea water, bottom sediments from ocean and estuarines	26°C-27°C and pH 7.6-7.7			78

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
pentachloronitrobenzene			Aspergellus niger, Flisarium solani, Clomerella congalate, Helmintaosporium victoreae, Myrotheum, Penicillium sp., Trichoderma veridae	Aerobic, only during active growth			57
phorate sulfate	Sulfoxide reduction		Soil bacteria	Anaerobic			57
toxaphene			Corynibacterium pyrogenes	Anaerobic			57
atrazine	Detoxification		BI-CHEM POB-6	Detoxsol saturated soils			59
Miscellaneous Hydrocarbons							
chemical waste			PHENOBAC, a mixture of aerobic and facultative micro-organisms	Aeration tank, pH 5.5-6.0,	100-600 mg/1 BOD, 3-75 mg/1 phenols	Plant under control in 15 days. 90-95% BOD reduction, 12 hrs.	114
crude petroleum products	Biodegradation	Non-toxic byproducts	Microorganisms	Contaminated soils and aquatic environments			28, 66
detergents (nonionic, anionic, cationic)			BI-CHEM TEX-4				59
ethoxylated phenols			BI-CHEM TEX-4				59
foams			BI-CHEM TEX-4				59
halogenated hydrocarbons	Biodegradation	Non-toxic byproducts	Microorganisms BI-CHEM POB-6 BI-CHEM PEP-7 BI-CHEM POC-3	Contaminated soils, aquatic systems			28 59 59 59
endosulfan		Endosulfan, endodiol endohydroether	Fungi, soil bacteria, actinomyces	Aerobic, 22° to 27°C	1 ug/ml	Fungi 90%, 6 weeks	57
	Degradation	Endosulfate (fungi), endodiol (bacteria) and CO_2, endohydroxy ether, and 2 unidentified products	Sixteen fungi, fifteen bacteria, three actinomyces species			Bacteria 70-80%, 10 days; actinomyates 30%, 10 days	70
endrin	Anaerobic degradation		Anaerobic digester sludge	Anaerobic, 35°C	150 ug/ml	100% 30 days	42
		Aldehydes and ketones with 5 to 6 chlorine atoms	Pseudomonas sp., Micrococcus sp., yeast, soil organisms	Aerobic			57
		Ketoendrin (24, 4%)	Fish pond algae				78
heptachlor	Anaerobic degradation		Anaerobic digester sludge	Anaerobic, 35°C	150 ug/ml	100%, 20 minutes	42
heptachlor epoxide	Anaerobic degradation		Activated digester sludge	Anaerobic, 35°C	150 ug/ml	50%, 60 days	42
heptachlorobornane		Hexachlorobornane	Micromonospore chalcae, bovine rumen fluid	Aerobic Anaerobic			57
kepone	Cometabolism		Treatment lagoon sludge	Anaerobic			57

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
lindane	Anaerobic degradation		Anaerobic digester sludge	Anaerobic, 35°C	150 ug/ml	100% 23 days	42
			Chlorella vulgaris,	Anaerobic (?)			57
		Pentachlorocyclohexane	Chlamydomonas reinhardtii	Aerobic			57
			Chlosteridium sp., Pseudomonas sp.	Anaerobic			57
		gamma-3,4,5,67-tetrachloro-1-cyclohexane, alpha BHC	Soil bacteria	Anaerobic			57
			Sewage sludge	Anaerobic			57
industrial surfactants	Biodegradation	Non-toxic byproducts	Microorganisms	Contaminated soils, aquatic systems			28
oil			BI-CHEM FOG-3				59
	Biodegradation		PHENOBAC	Aeration basin 0.5 MGD waste-water treatment at marine bulk liquid storage facility	Oil/grease 500 to 600 mg/l	81% 24 hrs 93% 72 hrs reduced to 7 mg/l	114
organic solvents	Biodegradation	Non-toxic byproducts	Microorganisms	Contaminated soils, aquatic systems			28
pesticides & herbicides	Biodegradation	Non-toxic byproducts	Microorganisms	Contaminated soils, aquatic systems			28
petroleum distillate			BI-CHEM SUS-8, detoxsol	4 acres contaminated soil	1,200 ppm	1 ppm, 21 days	59
phenolics	Biodegradation	Non-toxic byproducts	Microorganisms	Contaminated soils, aquatic systems			28
			BI-CHEM COG-2				59
polycyclic aromatic hydrocarbons	Biodegradation	Non-toxic byproducts	Microorganisms				28
polychlorinated biphenyls	Biodegradation	Non-toxic byproducts	Microorganisms				28
			BI-CHEM FOB-6				59
polynuclear aromatics			BI-CHEM FOG-6				59
refined petroleum products	Biodegradation	Non-toxic byproducts	Microorganisms				28, 66
sludges (paper industry fish and vegetable processing)			BI-CHEM PAC-5				59
sulfur compounds			BI-CHEM SUS-8				26
waste oil	Degradation		PHENOBAC, PETROBAC	4 million gallon lagoon POLYBAC N (macronutrients nitrogen and phosphorous)	800 ppm	99%, 9 months	114

SUBSTRATE	BIOLOGICAL ACTIVITY	PRODUCTS	BIOLOGICAL AGENT(S)	SPECIAL ENVIRONMENTAL REQUIREMENTS	INITIAL SUBSTRATE CONCENTRATION	CONTACT TIME	REFERENCES
lindane	Anaerobic degradation		Anaerobic digester sludge	Anaerobic, 35°C	150 ug/ml	100% 25 days	42
			Chlorella vulgaris,	Anaerobic (?)			57
		Pentachlorocyclohexane	Chlamydamonas reinhardtii	Aerobic			57
			Chlosteridium sp., Pseudomonas sp.	Anaerobic			57
		gamma-3,4,5,67-tetrachloro-1-cyclohexane, alpha BHC	Soil bacteria	Anaerobic			57
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